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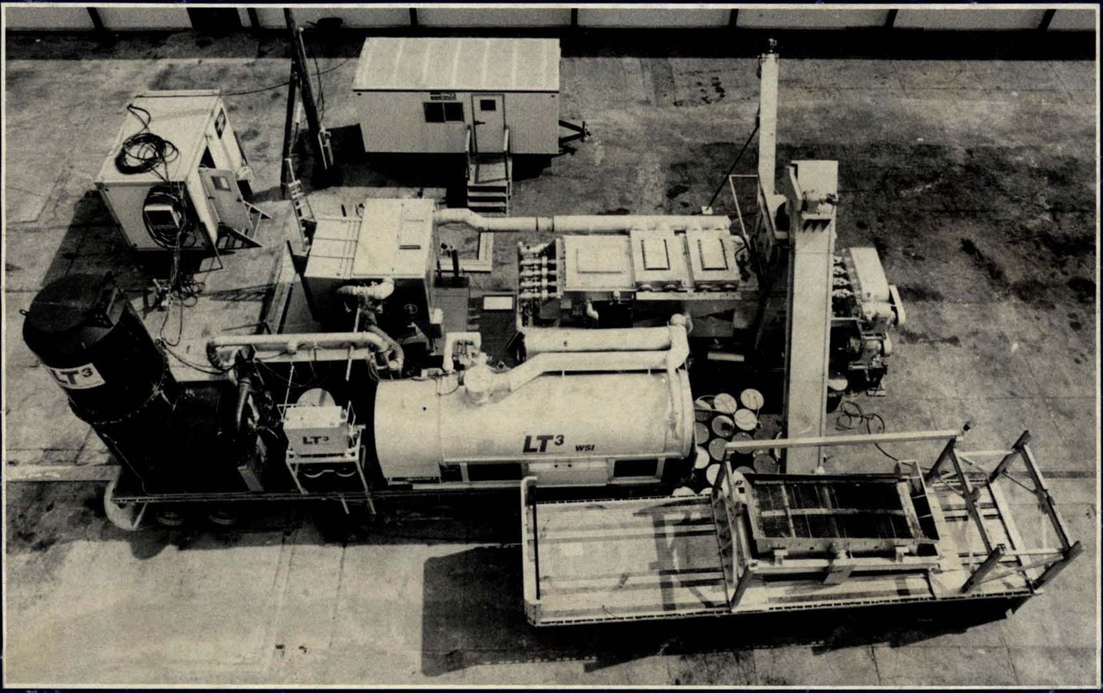
ENVIRONMENTAL PROGRESS



Full scale low temperature thermal treatment (LT^3) system installed and operational at the Illinois Department of Revenue site, Springfield, IL. (See article on page 139). Photo courtesy of Roger K. Nielson, Weston Service Inc., West Chester, PA.

ENVIRONMENTAL PROGRESS

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

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Editorial

Suggestions for Improving the Effectiveness of Environmental Laws And Regulations

Walter C. Barber

The legislative and regulatory framework for environmental protection in the United States does not always promote timely and efficient remediation of environmental problems. Some programs have been significantly more successful than others. The more successful programs tend to be characterized by explicit strategies, adequate resources, available technology and feasible objectives. The less successful programs tend to be hampered by weak science, infeasible objectives (e.g., zero risk), and poorly articulated strategies.

No one likes pollution or its effects. For more than twenty years the nation has struggled with the dual problems of correcting past practices and stimulating changes in behavior which result in a cleaner and safer environment. In some cases we have accomplished significant change in a relatively short period of time. In others we have made little progress despite extensive rhetoric and significant expenditures of human and financial resources.

Initial efforts to clean up the air, land and water were focused on large, visible and relatively easily corrected sources such as raw sewage discharges, power plants and other large sources of visible emissions, oil spills and litter. The federal government paid for sewage treatment plants, particulate emissions were reduced by shifting to low cost oil or installing relatively inexpensive equipment. Oil spills and litter were easily controlled through simple, virtually cost free, preventive measures. The consumer didn't see the bill.

Over time the problems have become more difficult as the public's appetite for better living has put more cars on the highways and more chemicals in commerce. The challenge has been compounded by the remarkable strides made by analytical chemists who have improved, by orders of magnitude, our ability to detect chemicals in air, water and soils. What seemed to be relatively simple and solvable problems in the 1960s have become extraordinarily complex, both technically and politically. The simple, easily affordable elimination of risk contemplated in the early air and water legislation have been made infeasible by science which has been unable to establish absolutely safe levels for exposure to many pollutants and which has developed methods to detect minute quantities of chemicals in the environment.

In the early 1970s, the environmental community generated support for new programs with expansive descriptions of risk and with little discussion of the cost to eliminate it. EPA and others voiced the opinion that 90% of cancer was the product of environmental exposure. Advocates of increased legislative and regulatory control frequently neglected to note that this estimate included and, in fact, was dominated by such "environmental" factors as smoking, alcohol, diet and exposure to sunlight. The public was left with the erroneous impression that cancer could be virtually eradicated if "industry" would just spend a few of its profit dollars on cleanups and pollution control.

Poorly articulated objectives and infeasible strategies are frequently associated with unsuccessful programs. While the goal of a risk-free environment may seem to be politically satisfying, the total elimination of risk is infeasible. Given the inability of science to specify safe levels for exposure, environmental programs can only reduce or manage risks. The establishment of risk elimination goals such as that articulated under Section 112 of the Clean Air Act will lead to frustration and inaction unless feasible implementation strategies tied to risk reduction are prescribed.

Although theoretically feasible, some objectives are so impractical as to make them effectively infeasible. Universal attainment of the ambient ozone standard falls into this category. Given our current knowledge of technology, significant reductions in ozone levels will require massive financial investments and disruptive changes in social behavior in every major metropolitan area. A blanket mandate from Congress that fails to recognize the magnitude of the problem and the costs of its solution is doomed to frustration and failure.

Every successful environmental program has been founded on the application of technology to reduce discharges or remediate past problems. Programs for which a technology based strategy cannot be identified, cannot succeed.

There are not nearly enough financial or human resources available to achieve all of the goals which have been established in environmental legislation within the foreseeable future. Just the attainment of the ambient ozone standard and the remediation of all past land disposal problems would require hundreds of billions of dollars of public and private sector investment and expense. History says that the taxpayers and consumers will not foot a bill of this magnitude. Congress has already decided not to fund environmental programs such as municipal treatment plants, Superfund or remediation of government owned sites at levels adequate to eliminate these problems even in our lifetime. EPA has not been given more than a fraction of the staff necessary to implement the programs which have been assigned.

Environmental protection is a resource allocation problem. Failure to recognize this fact will certainly result in misdirected and wasted resources. The assignment of staff to pursue cancer risks on the order of 10^{-7} in the Superfund program necessarily results in ignoring risks hundreds of times greater in magnitude in areas such as toxic air emissions or indoor air pollution. It is certain that once spent, those dollars will not be available for the management of other environmental risks.

Perhaps as critical as funding is the availability of a trained and experienced professional staff. Nowhere is this more evident than in the Superfund program where industry, consultants and regulatory agencies compete for a very limited resource. In the more successful air and water pollution control programs, the nation has had a pool of talent which had developed through decades of professional training and field experience. No such history exists in the site remediation field. The problem is compounded by the extraordinary complexity and political sensitivity which has been incorporated into remediation programs. Junior engineers are asked routinely to make risk-balancing judgments which the senior staff of EPA has been unable to make in other program areas such as toxic air pollutants or pesticide regulation.

RECOMMENDATIONS

Separate Long-Term Goals From Short-Term Strategies in Environmental Legislation

Congress and the public will not accept open-ended schedules for environmental improvements, nor will they accept the significant relaxation required to make standard universally attainable. Firm, reasonably short schedules are needed to assure progress.

Use Incremental Control Strategies to Approach Major Problems

The erroneous assumption that environmental laws or rules must provide ultimate solutions to problems causes more problems than it is worth. Large problems should be approached incrementally with Congressional review at each phase to ensure that technical and economic assumptions remain valid.

Base Short-Term Strategies on Demonstrated Technologies

Significant reductions in discharges and risk are almost always available through broader application of best available technologies and practices. Explicit requirements for the expeditious application of available technology will achieve more benefits than protracted discussions of ultimate solutions based or hoped for future improvements in technology. We can always revisit emission limits as technology improves.

Establish Explicit Risk Management Objectives in Legislation and Regulations

Too much time is wasted debating how clean is clean issues. Congress should be more explicit in the establishment of clean-up goals and anticipated costs to avoid subsequent debates over the acceptability of economic impacts.

Establish Deminimus Risk Levels and Stop Spending Time and Money on Inconsequential Activities

It is irrational to ignore cancer risk in the 10^{-3}-10^{-4} range while spending billions of dollars and hundreds of work years on risks in the 10^{-6}-10^{-7} range. EPA and Congress should agree that risks to individuals smaller than 1×10^{-6} are deminimus, that risks greater than 1×10^{-4} are generally unacceptable and that risks falling in the range 10^{-4}-10^{-6} should be reduced to the extent technology is available and its cost is reasonable.

Reduce Complexity in Both Laws and Regulations

Both Congress and EPA have drifted into a system which tries to solve environmental problems with words rather than actions. The length and complexity of both legislation and regulations diverts thousands of man years and millions of dollars from the limited resource pool. In many cases, simple performance standards could be substituted for pages of rhetoric and volumes of interpretive guidance. While more simple rules may include some economic inefficiencies and miss a few opportunities, on balance the environment is almost certain to be better off if the rules produce more action and less litigation.

Recognize the Estimated Cost of Risk Reduction in Environmental Laws

Too frequently EPA is unwilling to adopt a rule or a program which appears unreasonably expensive while Congress and the public have expressed a willingness to spend more for less risk reduction in other areas.

Walter C. Barber is Vice President-Environmental Management and Administration of Chemical Waste Management Inc., Oak Brook, IL, responsible for Chemical Waste Management's environmental compliance, safety and health programs. He also directs the Company's Human Resources, Public Affairs and Community Relations activities.

He holds Bachelor's and Master's degrees in Civil Engineering from Syracuse University and Catholic University and a Master's degree in Public Administration from Syracuse University. Mr. Barber is a member of the American Society of Civil Engineers and was Director of the Air Pollution Control Association from 1981-1984.

Computer Column Editor for *Environmental Progress*

Dr. Ashok Kumar is the editor of our new software column. He is Associate Professor of Civil Engineering at The University of Toledo where he teaches courses on air pollution and conducts research in the area of air pollution modeling and monitoring. Before joining UT, he was associated with Syncrude Canada Ltd. as an atmospheric physicist where he developed, planned and conducted studies related to the dispersion of emissions from a tar stands plant. He received his Bachelor of Science (1970) from Aligarh University in India, his Masters of Science (1972) from the University of Ottawa, and his Doctoral Degree (1977) from the University of Waterloo, Canada. A registered professional engineer, he is a consultant to industrial organizations.

Report Identifies Number Of Operating Hazardous Waste Landfills in U.S. Raises Superfund Monies Question

Environmental Information, Ltd., Minneapolis, MN has identified 24 available commercial hazardous waste landfills operating in the United States.

According to a recent article in the consulting report *EI Digest, Industrial and Hazardous Waste Management*, there are only fifteen states that have hazardous waste landfills, with four states (California, Louisiana, Indiana and Illinois) each containing three landfills.

EI Digest Senior Editor Cary Perket said "The significance of this report is that 24 of the landfill facilities are congregated in 15 states. That leaves 35 states that will need to reach agreement by year-end with neighboring states on disposing their wastes if they want to maintain their Superfund monies." The study reports that the average lifetime of these facilities, is fifteen years. "The Superfund Act requires states to demonstrate by October 1989 that they have sufficient capacity. While our study suggests that, at current generating rates, there is adequate capacity for the next fifteen years, most states will need to address the long hauling distance issue and begin the approval process for interstate agreements," said Perket.

The article, "Hazardous Waste Landfills: A Summary of the Disposal Options in Waste Management," states that Chemical Waste Management, Inc. leads the corporate sector owning seven landfills located in Alabama, California, Illinois, Indiana, Louisiana, New York and Oregon. The company also owns the largest existing facility, located in Alabama, with potential disposal capacity of 20,000,000 cubic yards.

"Based on the survey and the research conducted for this report," said Perkett, "five landfills are independently owned and 19 will be owned and operated by eight major management companies. This is the most current estimate that we can provide. In terms of new landfills, Browning Ferris Industries is the only company that is likely in the near future to open a new landfill, the Last Chance Landfill in Colorado. Otherwise, there are numerous public siting efforts by state governments, but none that appear to be close to getting permitted."

Technical Society To Focus On CFC-Ozone Depletion Issue

One possible contributor of the "greenhouse effect"—ozone depletion resulting from the use of fluorocarbons will be the focus of one of America's leading technical societies this year.

The Institute of Environmental Sciences' meeting will examine the problem, progress, and possibilities involved in reducing the use of CFCs this month at its 35th Annual Meeting in Anaheim, CA.

"CFCs are used universally in cleaning parts, electronic components, refrigeration and plastic foam," says Quintin Phillips of Hewlett-Packard, general chairman of the meeting. "The restriction of their use represents a significant challenge for the engineering community."

The Institute of Environmental Sciences, based in Mt. Prospect, Illinois, has 4,200 members involved in a wide range of engineering disciplines. Several panel discussions will be held on CFCs involving users from aerospace, computer and equipment manufacturing industries, as well as a panel involving solvent suppliers. Several papers presented will be exploring alternatives to cleaning using CFCs.

All total the 35th Annual Technical Meeting will include 44 sessions and 13 tutorials. Other subjects to be covered include contamination control, design, test and evaluation, product reliability, computer modeling and energy issues.

Environmental Information, Ltd. is known for its annual publication, *Industrial and Hazardous Waste Management Firms*, a national directory that profiles over 4,300 environmental services. For more information write: Environmental Information Ltd., 7400 Metro Blvd., Suite 400, Minneapolis, MN 55435 or call (612) 831-2473.

Washington Environmental Newsletter

Pollution Prevention

Strong Congressional and EPA support for legislation aimed at waste minimization/reduction/prevention has made this issue one of the most discussed topics in Washington. The Pollution Prevention Act of 1989 (S.585) introduced by Senator Frank Lautenberg (D.NJ) has over 20 cosponsors and a slightly different version (H.R. 2800) introduced by Rep. Howard Wolpe has garnered support in the House with over 150 co-sponsors. The legislation requires EPA to establish a "Multimedia Pollution Prevention Office" to carry out the act and foster source reduction efforts.

Two recent actions at EPA, following several reports on waste reduction and prevention, are indications that the trend toward pollution prevention is gaining momentum. Even before these reports were issued, EPA had taken the initiative to form an Office of Pollution Prevention—an idea embodied in the proposed legislation, but at this point funding for this effort is limited. EPA's Science Advisory Board has concluded:

> "In addition to the current emphasis on federally mandated controls that are put in place to clean up pollutants *after* they have been generated, EPA must develop a strategy that emphasizes the reduction of pollutants *before* they are generated. A strategic shift in emphasis from control and cleanup to anticipation and prevention is absolutely essential to our future physical, environmental and economic health."

EPA faces the challenge of building nationwide support for these initial steps. If public and private resources shift from control to prevention, the country will be taking a positive step towards a cleaner environment.

As we reported in the Feb. '89 issue of Environmental Progress, AIChE, through its GPSC is an active participant, along with EPA and other organizations, in a group studying the feasibility of forming a public/private Pollution Prevention Institute. We are also looking at ways in which AIChE can become proactive in areas of chemical source reduction.

Oil Spill Cleanup Through Biodegradation?

EPA's Office of Research & Development convened a meeting of world-wide experts on using microorganisms to degrade oil spills. They concluded that there are naturally occurring microorganisms in the Prince William Sound environment that could be used to accelerate the rate of oil degradation. They recommended a number of short term tests in Alaska that could result in improved clean-up operations later this year. EPA is proceeding to act on these recommendations in coordination with other Federal agencies and the State of Alaska.

For additional information contact Dr. Martin Siegel at the address shown below.

This material was prepared by AIChE's Washington Representative, Siegel • Houston & Associates, Inc.
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Book Reviews

Numerical Groundwater Modeling Flow and Contaminant Migration, William C. Walton, Lewis Publishers, Inc., Chelsea, MI (1989) 272 pages + 3 computer diskettes, U.S. List Price: $84.00

The use of microcomputers for executing ground-water flow and contaminant transport models has grown substantially during the last few years. Relative to large mainframe systems, microcomputers are generally more accessible, more cost effective, and well suited for simple flow geometries and scoping calculations. The author, William C. Walton presents two programs, GWFL3D and GWTR3D, which are modifications and extensions of, and sequels to, the mainframe computer programs PLASM and RANDOM WALK. The two computer programs supplied in the text are tailored for the IBM PC and compatible microcomputers and are designed to simulate quasi-three dimensional ground-water flow and contaminant migration.

An introduction to the text and the two microcomputer programs which includes the executable files as well as the source codes is provided in chapter 1. Chapter 1 also discusses the available programs for compiling GWFL3D and GWTR3D (if desired) and the commercial software packages for producing graphs, contour maps, and 3-D plots from output data.

Chapters 2 and 3 discuss program operation and simulation techniques for the flow code GWFL3D. The program provides numerical spatial-water level and time-water level output options and simulates the following aquifier systems and facility features: constant or variable production well discharge or injection well recharge; water table, leaky artesian, and nonleaky artesian conditions; constant head, constant flux, and no-flow aquifer system boundaries; induced surface water infiltration; ground-water evapotranspiration; aquifer storativity conversion; and multi-aquifer conditions.

Operation and simulation techniques for the transport code GWTR3D is discussed in chapters 4 and 5. GWTR3D simulates solute transport in ground-water (one, two or quasi-three dimensional), using random walk techniques. The program simulates continuous and slug sources, contaminant sinks, vertically averaged salt-water fronts, and contaminant leakage from overlying source beds. Processes of contaminant sorption and decay can also be simulated.

Five appendices are provided in the text. Appendix A lists the source code for GWFL3D and Appendix B lists the source code for GWTR3D. Appendix C describes the instructions for using the computer diskettes. Appendix D addresses the topic of modeling capability limitations to prevent potential program misuse. Appendix E presents two examples of input and output displays to guide the user through program operation.

The text is well structured and easy to read. Emphasis is placed on practice rather than theory. The subject matter of the book is presented in a fairly nonmathematical manner. The book is recommended for the practicing hydrologist, geologist, civil and environmental engineer, water well contractors, educators and students and others interested in numerical groundwater modeling.

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Underground Tank Leak Detection Methods. Shahzad Niaki and John A. Broscious, Noya Data Corporation, Park Ridge, NJ, 1987, U.S. List Price: $36.00

Currently there is a great deal of interest in detecting and preventing leaks from underground storage tanks. The subject of leak detection is important for regulatory agencies and for owners and operators of such tanks. Leak detection includes a number of topics: in-tank testing, inventory monitoring, external monitoring, line leak detectors, and interstitial monitoring. Leak detection is an active and rapidly expanding field, with encouragement being provided by state and federal regulatory activity.

The book reviewed here is essentially a discussion of in-tank leak detection techniques and, in particular, volumetric tests. The title of the text is therefore somewhat misleading. The book is based on a U.S. Environmental Protection Agency report published in January 1986 and discusses the status of in-tank testing as of mid 1985.

Three major chapters contain: a 23 page discussion of variables that affect the accuracy of in-tank testing methods; a 67 page review of individual leak detection techniques (generally by vendor); and a 21 page summary, in tabular form, of issues related to the various tank-testing methods considered. The reviews of individual techniques generally follow a standard format. First, a description of the method is given based on information from the manufacturer. Next, a discussion is presented of how the method compensates for the effects of the various variables that affect testing. Finally, a series of brief comments is given on significant factors that relate to the test, based on the authors' engineering judgment.

The major value of this book is that it provides a summary of important factors that affect the accuracy of volumetric tests (and a discussion of individual volumetric tests) that is based on a consideration of these factors. However, the book does omit a significant factor that can affect the accuracy of volumetric tank tests, namely tank size. Size becomes a major factor affecting the accuracy of such tests for large tanks. The book gives very limited attention to external monitoring, inventory control, line leak detectors, and interstitial monitoring. A reader interested in these topics will need to consult other sources.

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PC-SARA: A Software for Emergency Planning and Analysis

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Complying with environmental regulations is a part of daily activity for chemical plants. The fines for non-compliance can be as much as $25,000 per day. Over 40 programs are now available to meet various requirements of the Superfund Amendment and Reauthorization Act (SARA) of 1986 [*1*].

PC-SARA is a software developed by Technology and Management Systems Inc., 99 S. Bedford Street, Suite 211, Burlington, MA 01803-5128 for emergency planning and analysis. The hardware requirements for PC-SARA are as follows:

i. IBM compatible personal computer with DOS 3.0 or higher operating system,
ii. 20 megabyte hard drive, and
iii. graphic adapter card and graphics monitor.

The software is designed to help industries and local communities in the United States comply with many of the requirements of SARA Title III. The software is capable of developing Tier One and Tier Two chemical inventory forms. The program is user friendly for entering and retrieving the information on chemicals. It is easy to print out forms. However, the companies should check with the U.S. Environmental Protection Agency for acceptability of computer generated forms.

The software incorporates subroutines that allow the user to draw maps of local communities, industrial plants and nearby buildings. The dispersion calculations for hazard analysis are displayed along with the maps. This is a useful feature for public relation type of activities. The software comes with a user manual [2]. The manual is well written and is divided into nine chapters: 1) Introduction, 2) Installation of PC-SARA, 3) PC-SARA Tutorial, 4) Data input by facilities, 5) Data input by communities, 6) PC-SARA map drawing, 7) Hazard analysis and data analysis, 8) Other PC-SARA features and 9) System specifications. Three appendices are incorporated in the manual. One appendix is devoted to error messages given by the program and their explanations. The second appendix is a list of supported printers. The third appendix explains the procedure to load the CAMEO chemical data base developed by the National Oceanic and Atmospheric Administration (NOAA).

The atmospheric dispersion model used for computing a hazard area is based on an USEPA publication [3]. Chemical releases from a fixed facility or a transportation accident scene are handled by the software. Three different concentration levels (LOC: Level of Concern Concentration, PEL: Personnel Exposure Limit Concentration and TLV: Threshold Limit Value Concentration) are used to obtain hazard contours under worst case situation. The meteorological conditions for the worst case scenario are from reference [3]. It is possible to change the values of wind speed, wind direction and atmospheric stability for dispersion calculations in the program.

The documentation is very helpful in learning and running the program. The important steps in using the program are explained using the actual information displayed on the computer screen. In order to review the software the demonstration disk supplied by the company was first run. No difficulties were encountered in using the disk. The demonstration clearly reflected the excellent capabilities of the PC-SARA software. After this step the main program was loaded following the steps given in the manual and the program was run for an ammonia solution spill. The program worked fine and displayed a hazard area for the spill. It used the chemical information stored during the "Edit Data" step. The changes to the map took some time. This step is a slightly lengthy process but is understandable due to the extreme care that must be taken in drawing to scale and siting various facilities that may be in the hazard area during a chemical spill. Several cases were run using different options built in the program.

The following minor problems were observed during this process:

i. When the main menu is displayed and choice number 5 is opted for, the computer "hangs up" instead of giving an error message that no chemical is defined as having been spilled. In this situation the computer has to be rebooted. However, for options 1, 2, 3, and 4 of the main menu, error messages are displayed by the program for the above situation. The errors can be corrected using the information given in the appendix. Therefore, care should be taken to input a chemical for hazard analysis before option 5 is chosen.

ii. Sometimes when a CAS #7664417 (for ammonia) was entered in the program, we surprisingly received an error message on the screen. After we tried to reenter the same CAS # 2-3 times, the map screen showed up with no map and then the whole screen went blank. In order to communicate with the program we had to press the F1 key and a help screen appeared but could not be utilized. The computer had to be rebooted to get out of this situation.

During our review we talked to the staff of the company and found them very helpful. They also told us that the new version of the program does not have the above problems and a mouse version of the program is available for use. Overall we found it an excellent software and the package will be very useful for SARA related activities.

References

1. McCarthy, L. R., "Compliance Software for Government and Industry," *Hazmat World*, pp. 30-33, Oct. 1988.
2. *Technology and Management Systems*, "PC-SARA User Manual," 1988.
3. *USEPA/FEMA/USDOT*, "Emergency Planning for Extremely Hazardous Substances," Washington, D.C., 1987.

SKYGAS REPORT

New Waste Disposal Technology

Breakthrough Process Converts Solid and Semi-Solid Wastes Into Clean Burning Medium BTU Gas

Do you have a waste disposal problem? Would you like to convert your waste into energy? If so, you should check out Skygas. It's a new electrokinetic process that makes use of free radicals to quickly and efficiently gasify any carbonaceous feedstock. Commercial applications are scheduled to begin in late 1989.

A prototype Skygas unit (5 tons/hour) is currently being used as a test bed for gasifying a variety of feed materials: municipal solid waste (MSW), dewatered municipal sewage sludge (MSS), wood chips and hogwood, biomass and agricultural residues such as rice straw, high sulfur coal, and petroleum coke piggybacked with refinery wastes. A small batch unit is also available for fast screening studies.

Feed materials to be tested in the near future include medical and infectious wastes, printed circuit boards, pulp and paper mill wastes, and animal wastes.

Why does Skygas make sense? Because preliminary tests show that this process is much more economical than mass incineration. Plus, Skygas appears to be environmentally far superior. Stack emissions produced by conventional burning are difficult and expensive to deal with. But with Skygas, since there is no air or oxygen used in the process, the gas is relatively easy to clean. The typical product gas contains more than 90% hydrogen and carbon monoxide, and has very little, if any, carbon dioxide in it.

The gas produced by Skygas can be burned to make steam or electric power. The composition of this gas also makes it a very useful building block for downstream conversion into chemicals such as methanol and ammonia.

Even with limited exposure, interest in Skygas has been widespread. In the U.S., most of us are aware that waste problems have reached crisis proportions. Thus, we were not surprised to find that a majority of our Skygas inquiries from North America focus on safe, efficient disposal as the primary objective. Developing countries have expressed special interest in the power generating aspects of the technology.

If you have commercial or financial interest in Skygas, write to us on your letterhead. We will send you more information and a status report. No phone calls please. Inquiries from foreign governments and agencies are welcome. Contact:

Technology Resources & Services
P.O. Box 487 • Glenview, Illinois 60025, U.S.A.
Attn: Skygas Program Manager

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Anaerobic Treatment of Pulp and Paper Mill Wastewaters

John W. Lee Jr. and David L. Peterson
Ch2M Hill Inc., Bellevue, Washington
and
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Canviro Consultants, Waterloo, Ontario, Canada

Secondary treatment of pulp and paper mill wastewaters for biochemical oxygen demand (BOD) removal worldwide has traditionally been accomplished, and particularly in North America, by aerobic treatment processes, including aerated stabilization basin and activated sludge. In recent years, however, interest in applying anaerobic processes to treat pulp and paper mill effluents has increased, with at least 25 full-scale installations currently operating or under construction.

INTRODUCTION

Renewed interest in anaerobic processes in North America is perhaps the most exciting industrial waste treatment development to occur since the wide application of the activated sludge process to meet industry categorical effluent standards mandated by the Clean Water Act of 1972 (PL 92-500). The use of anaerobic processes for stabilization of biodegradable organics allows waste treatment to be coupled with energy production, affording the opportunity to minimize operating costs and even the potential for some return on capital investment. Both the characteristics and quantity of biodegradable organic compounds in pulp and paper mill effluents make anaerobic treatment an economically attractive alternative to the aerobic treatment processes traditionally used.

Anaerobic digestion of municipal sewage sludge has been practiced routinely since the 1930s. Until the present decade, however, anaerobic treatment of industrial wastewaters has been limited primarily to the poultry and red meat packing and vegetable processing industries. Anaerobic lagoons were first used in Australia in 1940, but little full-scale use was made in the food processing industry in the United States until 1955 [*1*].

The potential for anaerobic treatment of high strength, readily degradable organic wastes has long been recognized in theory, if not in practice. In anaerobic processes, organics are oxidized to carbon dioxide (CO_2) and reduced to methane (CH_4). Since an electron acceptor (i.e., oxygen) is not provided, the energy conservation required for this simultaneous oxidation and reduction process gives it several unique advantages, but it also has some limitations compared with aerobic treatment. The advantages are:

- Lower production of biosolids per unit of organics (i.e., BOD_5, COD, TOC) removed—typically 1/3 to 1/5 that of aerobic treatment of similar substrates.
- Lower requirements for inorganic nutrients ((nitrogen and phosphorous) as a consequence of less biosolids produced—anaerobically produced volatile biomass is typically about 11% nitrogen and 2% phosphorous.
- No aeration is required, significantly reducing overall treatment system power requirements.
- The methane produced is recoverable as a by-product fuel source—typically 0.35 std m3/kg COD removed.
- Anaerobic systems can be left dormant without feed for long periods of time (12 to 18 months) without severe deterioration in biomass properties, and can be brought back into service at normal treatment efficiency within very short periods of time (typically 1 to 3 days).
- Very high active biomass densities (1% to 3% and higher) can be achieved under favorable conditions in anaerobic reactors.
- Increased resistance to organic shock loads.

Limitations of the process include:

- Lower substrate removal rates per unit of biomass—typically 1/4 to 1/10 those for aerobic treatment of similar substrates.
- Both the lower substrate removal rates and the lower sludge yields can result in significantly longer times for initial system startup and for recovery after an upset (1 to 6 months).
- The lower biosolids yield, typically 0.04 to 0.08 pounds TSS per pound COD removed, makes biosolids retention increasingly critical as waste strength declines, in order to maintain adequate biomass in the treatment system.
- The chemically reduced conditions necessary for anaerobic processes produce compounds, including hydrogen sulfide, mercaptans, organic acids, and aldehydes, that are both malodorous and corrosive.
- Sensitivity to certain inhibitory and toxic compounds, such as oxidants (O_2, H_2O_2, and Cl_2), H_2S,

HCN, SO_3^-, and high concentrations of certain wood extractives, including resin acids.

Attempts in the 1950s and 1960s to use anaerobic processes to treat pulp and paper mill effluents, as well as other industrial wastes, gained anaerobic treatment a tarnished reputation because it did not perform as anticipated. Many of the problems resulted from a lack of understanding of the biochemistry and microbiology of anaerobic processes and from inexperience with translating these fundamental concepts into reliable, large-scale system designs.

Continued research and development in the 1970s and early 1980s resulted in significant advances in the state of the art of anaerobic treatment technology. These advances led to the successful use of full-scale anaerobic treatment systems in the pulp and paper industry. In 1978, Inland Container Corporation converted one of two existing aeration basins at a waste paper recycle mill into an anaerobic lagoon, thus achieving the first successful full-scale application of anaerobic treatment in North America and perhaps the world [2]. A full-scale anaerobic contact system to treat selected effluents from a sulfite mill was successfully started up and placed into operation at Hylte Bruk, Sweden, in late 1983 [3]; a similar system was developed for a semichemical pulp waste paper mill in Spain [4]; and for a sulfite pulp mill and cellulose derivative manufacturing facility in Sweden [5] in 1984. An anaerobic contact system put into operation by Niagara of Wisconsin in 1986 was the first high-rate, full-scale anaerobic facility at a North American pulp and paper mill [6].

The first full-scale operation of upflow anaerobic sludge blanket technology in the pulp and paper industry occurred at two wastepaper recycle mills in the Netherlands in 1983 [7]. The application of anaerobic treatment technologies in the pulp and paper industry is continuing to expand, such that at least 25 full-scale systems were operating or under construction in 1988.

APPLICABILITY OF ANAEROBIC TREATMENT TO PULP AND PAPER WASTEWATERS

Biochemical and Microbiological Considerations

Anaerobic biodegradation is a multistage process involving three basic groups of bacteria. Complex organic compounds are sequentially converted, through a series of intermediate compounds, to methane and carbon dioxide, as indicated by the four-step process shown in Figure 1.

Complex, high molecular weight, soluble organic compounds (i.e., carbohydrates, lipids and proteins) and particulates are usually the first to be hydrolyzed (Stage 1) to simple organics (i.e., simple sugars, amino acids, glycerol, and fatty acids). These simple organics are converted by acid-forming bacteria to higher organic acids (such as propionic and butyric acid), and to acetic acid, hydrogen, and carbon dioxide in a fermentation or acidogenic phase (Stage 2). The higher organic acids are subsequently converted to acetic acid and hydrogen (Stage 3) by acetogenic bacteria. The acidogenic and acetogenic bacteria belong to a large, diverse group that includes both facultative and strict anaerobes [*1*]. The wastewater characteristics determine which bacteria predominate.

The final step (Stage 4) to produce methane is carried out by three groups of methane bacteria: *Methano-bacterium, Methanoscarcina*, and *Methanococcus*. These strict anaerobes are capable of metabolizing formic acid, methanol, and carbon monoxide, as well as acetic acid, hydrogen, and carbon dioxide, to methane.

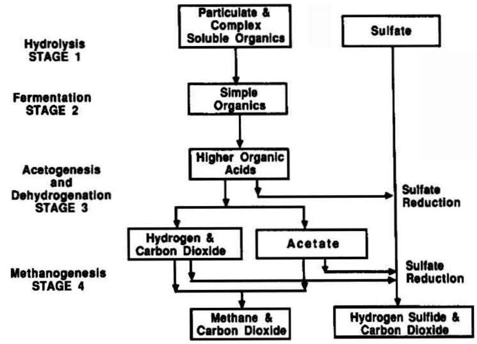

Figure 1. The four stages of anaerobic metabolism to methane in competition with sulfate reduction.

In anaerobic processes where inorganic sulfur is a constituent of the wastewater, the sulfate-reducing bacteria, *Desulfovibreo*, are also of importance [*1*]. Sulfate and/or sulfite is present in most effluents from acid sulfite, neutral sulfite semi-chemical (NSSC), kraft, chemimechanical (CMP), and chemithermomechanical (CTMP) pulp mills, and where aluminum sulfate is used as a sizing agent for paper production. The sulfur-reducing bacteria use sulfate and sulfite as electron acceptors in the metabolism of organic compounds to produce hydrogen sulfide and carbon dioxide as end products. Sulfur reduction can become a significant factor in the performance and operation of anaerobic treatment of pulp and paper mill effluent. The hydrogen sulfide produced can be both toxic and corrosive. As shown in Figure 1, the sulfur-reducing bacteria use the same organic compounds as do the methane bacteria, reducing methane yield per unit of substrate removed.

Wastewater Characteristics and Treatability

The pulping of wood or other cellulosic materials, whether it is done mechanically or chemically, results in the solubilization of organic materials such as lignin and various wood extractions, including carbohydrates, acetic and other organic acids, methanol and other low molecular weight alcohols, and a small amount of inorganic ash. Typical chemical characteristics for wastewaters from a hardboard mill using thermomechanical pulping (TMP) are summarized in Table 1.

Lignin is quite refractory to biological degradation. Carbohydrates, uronic acids (composed of xylose units, i.e., wood sugars), and the acetyl groups (organic acids), however, are very easily metabolized under both aerobic and anaerobic conditions. As indicated in Table 1, these compounds make up 40 to 60 percent of the total organics released into pulp and paper mill effluents.

Environment Canada's Wastewater Technology Centre recently conducted a screening study of 42 in-plant waste

TABLE 1. CHARACTERISTICS OF TMP HARDBOARD PULP MILL EFFLUENTS [9]

	Chemical Characterization (As Percent Total Dry Solids)			
Parameter	Whitewaters			Total Mill Effluent
Total Lignin	16.1	23.0	17.3	25
Carbohydrates	42.0	46.8	56.1	16
Uronic Acids	7.5	8.3	7.8	8
Acetyl Groups	2.2	2.6	2.5	4
Ash	6.0	5.2	2.9	30
Uncharacterized	24.0	14.1	23.4	13

TABLE 2. PULP AND PAPER MILL PROCESS STREAMS SUITABLE FOR ANAEROBIC TREATMENT [10]

Kraft Mills	Thermomechanical Mills
Woodroom	Final Effluent
Stripper Feed	Chip Wash
Contaminated Hot Water	Clarifier Effluent
Evaporator Condensate	Chemithermomechanical Pulp
	Thermomechanical Pulp
Sulfite Mills	Thermomechanical Pulp Linerboard
Neutral Sulfite Semi-Chemical Spent Liquor	**Non-Sulfur Semi-Chemical Mills**
Final Effluent	
Clarifier Effluent	Controlled Effluent
Combined Sewer Effluent	Clarifier Effluent
Acid Condensate (hardwood)	
Washer (softwood)	

streams from 21 Canadian pulp and paper mills, to assess their potential amenability to anaerobic treatment [8]. The screening process consisted of chemical characterization (COD, BOD_5, VSS, and sulfate) and an anaerobic serum bottle technique to demonstrate biodegradability. Twenty-three (55 percent) of the various effluent streams (Table 2), from kraft, sulfite, mechanical, and semi-chemical mills, were found to be suitable for anaerobic treatment. With adaptation and/or removal of inhibitory factors, other process streams may also be effectively treated under anaerobic conditions.

Chemical, biochemical, and physical properties of some mechanical, chemimechanical, chemical pulping, and pulp bleaching effluents that have been successfully anaerobically treated in pilot studies or at full-scale are summarized in Tables 3, 4, and 5. A significant fraction of the organics in these effluents are either organic acids or alcohols. As illustrated in Figure 1, anaerobic degradation of these compounds bypasses the first two stages (hydrolysis and acidogenesis), and they are converted, through acetogenesis and dehydrogeneration (Stage 3), to the methane precursors (acetate, hydrogen, and carbon dioxide). Formic acid, acetic acid, and methanol are converted directly to methane by the methanogenic bacteria.

FACTORS TO BE CONSIDERED IN APPLYING ANAEROBIC PROCESSES TO TREAT PULP AND PAPER WASTEWATERS

Some of the factors to be considered in applying anaerobic processes to treat process effluents from pulp and paper mills include:

Treatment process kinetics (i.e., substrate removal, production of excess biomass, temperature)
Production rate and composition of the biogas produced
Requirements for inorganic nutrients

TABLE 3. CHARACTERISTICS OF MECHANICAL AND CHEMIMECHANICAL PULPING EFFLUENTS

	Pulping Process		
Parameter*	TMP Ref. (11)	TMP Ref. (12)	CTMP Ref. (13)
Total COD	5,600	7,210	6,000-9,000
Total BOD_5	2,800	2,800	3,000-4,000
BOD_5/COD	0.50	0.39	0.44-0.50
Carbohydrates	1,230	2,700	1,000
Acetic Acid	—	235	1,500
Methanol	—	25	—
TSS	810	383	500
VSS	660	—	—
Total Nitrogen (as N)		12	—
Total Phosphorus (as P)		2.3	—
Total Inorganic Sulfur (as S)		72	167
pH	4.2	—	

*Units of all parameters are mg/l, except pH.

TABLE 4. CHARACTERISTICS OF CHEMICAL PULPING CONDENSATES

	Acid Sulfite Condensate		Kraft Foul Condensate		
Parameter*	Ref. (14)	Ref. (15)	Ref. (16)	Ref. (17)	Ref. (18)
Total COD	4,000-8,000	9,800-27,100	16,000	1,202	10,00-13,000
Total BOD_5	2,000-4,000	3,700-5,110	10,700	568	5,500-8,500
BOD_5/COD	0.5	0.19-0.38	0.67	0.47	0.55-0.65
Total Volatile Acids (as HAC)**	3,650	—	16	5.4	30-300
Methanol	250	—	—	421	7,500-8,500
Ethanol	—	—	—	5.8	—
2-Propanol	—	—	—	18.2	—
Furfural	250	—	—	—	—
Acetone	—	—	—	5.1	—
TSS	—	—	0	16	0
Total Nitrogen (as N)	—	—	306	—	350-600
Total Phosphorus (as P)	—	—	1.0	—	0.02-1.55
Total Inorganic Sulfur (as S)	800-850	840-1270	91	5.9	120-375
pH	2.5	2.8-5.9	10.2	8.0	9.5-10.5
Alkalinity (as $CaCO_3$)	—	—	1,060	31	2,130-2,660
Temperature (°C)	25-50	—	—	—	55-60

*Units of all parameters are mg/l, except pH and temperature.
**Includes acetic and formic acid.

TABLE 5. CHARACTERISTICS OF PULPING AND BLEACHING LIQUORS

Parameter*	NSSC Pulping (12)			Alkaline Semi-Chemical and Wastepaper Recycle Mill Effluent (4)	Bleached Kraft Caustic Extract (17)
	Spent Liquor	Chip Wash	Paper Mill Effluent		
Total COD	39,800	20,600	5,020	11,300-54,700	1,124-1,738
Total BOD_5	13,300	12,000	1,600	5,300-19,500	128-184
BOD_5/COD	0.33	0.58	0.32	0.36-0.47	0.11
Carbohydrates	6,210	3,210	610	—	—
Acetic Acid	3,200	820	54	—	0
Methanol	90	70	9	—	40-76
Ethanol	5	990	—	—	0
TSS	253	6,095	800	200-18,900	37-74
Total Nitrogen (as N)	55	86	11	—	—
Total Phosphorus (as P)	10	36	0.6	—	—
Total Sulfur (as S)	868	315	97	500	—
pH	—	—	—	—	10.1
Alkalinity (as $CaCO_3$)	—	—	—	—	275-755
Temperature (°C)	—	—	—	31.5-39.0	—

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*Units of all parameters are mg/l, except pH and temperature.

Effects of pH and alkalinity on treatment performance
Inhibition and toxicity effects

Treatment Kinetics

Substrate Removal: The rate of organics removal (i.e., kg BOD, COD, TOC removed per day) depends upon the quantity of viable biomass available to facilitate metabolism and on intimate contact of the biomass with the substrate. The relationship of substrate removal to biomass is often termed the food-to-microorganism or food-to-biomass (F/M) ratio. Under conditions where the quantity of viable biomass is large compared with the amount of degradable organics applied (and therefore not a factor limiting substrate removal), treatment efficiency can be related to F/M by the following equation:

$$\frac{F_r}{M_v} = K\left(\frac{Se}{So}\right) \tag{1}$$

Where:
F_r = Substrate removed (kg/d)
M_v = Volatile biomass in contact with the substrate (kg)
K = Substrate removal rate constant (kg/kg-d)
Se = Soluble effluent substrate (i.e., BOD_5, degradable COD) concentration (mg/l)
So = Total influent substrate (i.e., BOD_5, degradable COD) concentration (mg/l)

The value of K for anaerobic treatment of pulp and paper mill effluents is in the range of 2 to 5 kg BOD_5 removed/kg VSS/day at 35 degrees C (6). K values fall within the range of 7 to 17 for aerobic treatment of similar wastes [*19*]. To achieve similar treatment efficiencies, anaerobic systems need approximately 3 to 4 times the biomass of aerobic systems. For this reason, the focus of anaerobic treatment application in pulp and paper and in other industries has been as a pre-treatment step for organic load reduction rather than a single-stage system to achieve high-quality effluent. Subsequent aerobic polishing can achieve low soluble substrate concentrations in the final effluent as well as very high overall treatment efficiencies, approaching 99 percent [20].

Biomass Yield: The yield of biomass produced from aerobic as well as anaerobic degradation of organic matter is expressed by the following equation:

$$VSS_p = a(F_r) - b\,(M_v) \tag{2}$$

Where:
VSS_p = Quantity of excess volatile biomass produced (kg/d)
a = Quantity of volatile biomass initially synthesized from soluble substrate (kg/kg)
F_r = Substrate removed (kg COD, BOD_5, TOC removed/day)
b = Fraction of biomass endogenously metabolized (kg/kg-day)
M_v = Quantity of volatile biomass in contact with the substrate (kg)

This equation is often rearranged by dividing through by M_v to relate the sludge age (ϕ_c), or average length of time the biomass remains in the system, to F_r/M_v.

$$\frac{1}{\text{Sludge Age } (\phi_c)} = \frac{VSS_p}{M_v} = a\left(\frac{F_r}{M_v}\right) - b \tag{3}$$

The values assigned to the biosolids synthesis and endogenous constants "a" and "b" depend largely on substrate composition. In the literature reviewed for this paper, no data were found where values for the constants "a" and "b" had specifically been determined for pulp and paper mill effluents. Based on data development from other wastes containing organic acids and carbohydrates (two constituents found in wood extractive from both mechanical and chemical pulping), the biosolids yield coefficients are expected to be in the following ranges [21]:

	Synthesis Coefficient, a ($mg\ VSS_p/mg\ COD_r$)*	Endogenous Coefficient, b ($mg\ VSS_d/mg\ VSS$ day)*
Carbohydrates	0.10 - 0.18	0.02 - 0.03
Acetic Acid	0.04 - 0.06	0.011 - 0.015
Mixed Organic Acids	0.04 - 0.06	0.015

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*VSS_p - VSS produced, VSS_d - VSS destroyed, COD_r - COD removed.

These values for the synthesis and endogenous coefficients for anaerobic conditions are on the order of one-third of those found for pulp and paper mill wastes treated aerobically [*19*]. Thus, for similar sludge age operating conditions, the excess biomass yield is on the order of one-third of that of aerobic processes.

Temperature: The metabolic rate of all biological systems is affected by temperature. Biochemical reactions proceed more rapidly with increasing temperature. The treatment efficiency of anaerobic processes compared with aerobic processes is particularly sensitive to operation below optimum temperatures, because of the significantly lower substrate removal rate constants discussed above.

Considering the relatively high temperatures of many pulp and paper mill process streams (50 to 85 degrees C), operation of anaerobic treatment systems in the optimum range of 55 to 60 degrees C for thermophilic bacteria has been investigated, but as yet has not been found to be effective. To the authors' knowledge, all of the full-scale anaerobic systems currently treating pulp and paper mill effluents are operating in the mesophilic temperature range, where the optimum temperature is 32 to 36 degrees C. The reduction in treatment efficiency with decreasing temperature can be determined from the following Arrhenius relationship for chemical reactions:

$$\frac{K_2}{K_1} = \phi_T^{T_2-T_1} \qquad (4)$$

Where:

K_1 and K_2 = Substrate removal rate coefficient at temperature T_1 and T_2 (degrees C)

ϕ_T = Temperature coefficient

Although no data were found in the literature for a value of ϕ_T for anaerobic treatment of pulp and paper mill effluents, it is assumed to be about 1.05, based on the classic sewage sludge anaerobic digestion studies of Fair and Moore in 1937, which correlated gas production and retention time with temperature [*1*].

Biogas Production and Composition

Methane and carbon dioxide gas produced from anaerobic metabolism of organic compounds can be estimated by the following equations developed by Buswell [*42*].

$$C_n H_a O_b + \left(n - \frac{a}{4} - \frac{b}{2}\right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} - \frac{b}{4}\right) CO_2 + \left(\frac{n}{2} - \frac{a}{8} - \frac{b}{4}\right) CH_4 \qquad (5)$$

At standard conditions of temperature (273 degrees K) and pressure (1 ATM), 0.35 m^3 methane will be produced for every kg of COD removed. Methane is insoluble in water, while carbon dioxide is very soluble and readily converted to bicarbonate alkalinity, depending upon the pH and the cations available for ionic balance. Thus, the carbon dioxide content of the biogas will depend both on the chemical composition of the substrate and on the reactor pH. The carbon dioxide content will decrease with increasing pH.

In addition to potential hydrogen sulfide toxicity, the amounts of sulfate and sulfite present in pulp mill effluents can significantly affect the overall economics by reducing methane gas generation. This is due to anaerobic bacterial reduction of sulfate and sulfite (two inorganic sulfur compounds present in many process effluents from chemical and chemimechanical pulping). While sulfur-reducing and methanogenic bacteria compete for the same energy sources (acetic acid and hydrogen produced by acid-forming and acetogenic bacteria), the sulfur reducers are energetically favored, as indicated by the comparison of energy yield at standard conditions [23] (See below.)

Methanogenesis:

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3\,H_2O \qquad - 135.9\ \text{kJ/reaction}$$

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \qquad - 31.0\ \text{jK/reaction}$$

Sulfate Reduction:

$$H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + H_2O \qquad - 152.6\ \text{kJ/reaction}$$

$$CH_4COO^- + SO_4^{2-} \rightarrow HS^- + 2\,HCO_3^- \qquad - 71.7\ \text{kJ/reaction}$$

Two kg COD are required to reduce one kg of sulfate or sulfite (as sulfur). Thus, methane yield is reduced by 0.7 m^3 for every kg of sulfur reduced.

Nutrient Requirements

Inorganic nitrogen and phosphorus are required as macronutrients for biomass synthesis in all biological treatment processes. The necessary quantities are in proportion to the net biomass produced, considering both initial biomass synthesis and endogenous respiration. For anaerobic biomass, the nitrogen requirement is approximately 11 percent of the net cell weight, based on an empirical cell composition of $C_5H_9NO_3$ where phosphorus is approximately 2 percent of the biomass [22].

Pulp and paper mill effluents are characteristically devoid of phosphorus and nitrogen, unless these inorganic elements are used in the pulping process (i.e., ammonia-based acid sulfite) or paper making (ammonium sulfate sizing). The lower biosolids yield resulting from anaerobic treatment can reduce the requirement for supplemental nitrogen and phosphorus addition to one-third or less of that required for aerobic treatment.

In addition to nitrogen and phosphorus, several other inorganic constituents are required in trace quantities for optimum functioning of anaerobic processes. These micronutrients include iron and nickel (1 to 5 ppm), cobalt, molydenum and selenium (approximately 0.05 ppm). Some or all of these trace nutrients may be available in adequate amounts in the raw water supplied to pulp and paper mills, and as a result of piping and equipment corrosion. However, for effective anaerobic treatment of distillate effluents, such as condensate from spent pulping liquor evaporation, micronutrient addition is essential.

pH and Alkalinity

The optimum pH range for maximizing methane production is generally between 7.0 and 7.5, although acclimation to pH conditions outside this range over a long period of time is possible. Methane gas production will begin to drop below a pH of 6.5 to 6.8 as a result of methane bacteria growth inhibition. Below pH 6.0 and above 8.5 to 9, methane gas production may cease altogether.

Bicarbonate alkalinity is the primary buffer for maintaining pH, since carbon dioxide is released as an end product of anaerobic degradation. Alkalinity addition (lime, soda ash, or caustic) is necessary unless cations that can react with carbon dioxide to form a bicarbonate buffer are released during metabolism. Degradation of organic acid salts (i.e., sodium acetate) releases cations when the organic acids are metabolized. Alcohols, aldehydes, and carbohydrates are neutral compounds without the cations. Alkalinity from another source must provide the buffer necessary to neutralize the organic acids produced during acidogenic metabolism of these compounds. Bicarbonate alkalinity in the range of 1,000 to 1,500 mg/l ($CaCO_3$) normally is adequate to maintain a near-neutral pH. The composition of pulp and paper mill effluents can include organic acids, salts of organic acids, alcohols, aldehydes, ketones, and carbohydrates. The necessity for supplemental alkalinity will depend on the combination of process streams treated and the volatile acid concentrations maintained in the anaerobic digester.

Inhibition and Toxicity

Historically, anaerobic processes have been identified as being more sensitive than aerobic treatment to conditions or chemical constituents that are inhibitors or that are toxic. In general, however, there is no significant difference in toxics sensitivity between aerobic and anaerobic processes. Compounds that are aerobically degradable usually can be decomposed under anaerobic conditions as well [*24*]. Anaerobic bacteria have considerable capacity to acclimate to operating conditions and compounds otherwise considered to be inhibitory or toxic. However, because the growth rate of anaerobic compared with aerobic bacteria is much slower, toxic or inhibitory effects can last much longer.

The inhibitory or toxic compounds and conditions that are of potential concern in anaerobic treatment of pulp and paper process wastewaters include:

- Inorganic sulfur compounds (sulfate, sulfite, and sulfide)
- Oxidants, including hydrogen peroxide
- Volatile organic acids
- Heavy metals
- Wood extractives, including resin acids
- Organic additives, such as DPTA, a strong chelating agent

The toxicity of inorganic sulfur compounds increases in the order of sulfate $\leq$ thiosulfate $\leq$ sulfite $\leq$ sulfide [*25*]. Sulfate can be tolerated up to concentrations as high as 5 g/l [*26*]. Soluble H_2S concentrations above 50 mg/l can be inhibitory, but with some acclimation, soluble sulfides up to 200 mg/l can be tolerated [*27*].

Hydrogen sulfide dissociates in water in two steps. The species present depends on pH, as indicated in Figure 2. Undissociated H_2S is the most toxic sulfide species. Inhibition can be minimized by increasing pH, within the optimal performance limits, to accommodate a higher concentration of total sulfide ($H_2S + HS^-$). In the alternative, inorganic sulfur must be removed, as discussed in a later section of this paper. There is evidence that organic sulfur compounds in pulp and paper effluents, particularly lignosulfonates, do not decompose under anaerobic conditions [*28*]. Thus, it is only the reduction of inorganic sulfur to hydrogen sulfide that is of concern.

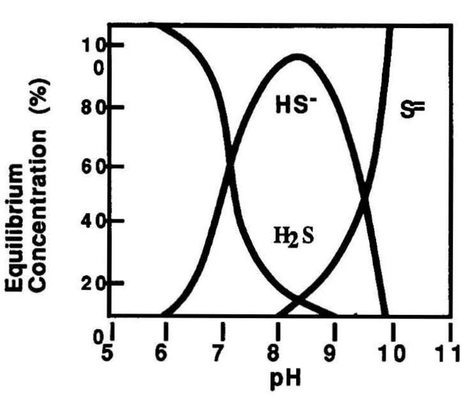

Figure 2. Sulfide species as a function of pH.

Methanogenic bacteria are strict anaerobes, requiring a highly reduced environment with optimal redox conditions of less than $E_c - 510$ MV [*29*]. Thus, oxygen and other oxidants present in the feed to anaerobic systems are toxic to the methanogens. Hydrogen peroxide, frequently used to bleach mechanical pulps, is of particular concern. While known to be toxic to bacteria in general (indeed, hydrogen peroxide is used for sterilization and disinfection), the obligate anaerobic bacteria lack the catalase enzyme necessary for peroxide decomposition. Thus, the methanogenic bacteria are especially sensitive to the presence of hydrogen peroxide.

The facultative acidogenic bacteria, however, do produce the catalase enzyme. Physical separation of the acidogenic and methanogenic phases of anaerobic metabolism (Figure 1) into two sequential stages is one method of peroxide detoxification [*13*]. Both the biocatalytic action of the acidogenic bacteria and the chemical reaction with reduced compounds cause peroxide to be decomposed. When anaerobic treatment is followed by activated sludge aerobic polishing, waste-activated sludge (which also contains facultative acid-forming bacteria) can be combined with a hydrogen peroxide-laden effluent in a detoxification pretreatment stage, prior to single-stage anaerobic treatment [*13*] [*6*].

Volatile acids can be toxic by virtue of their acidity above about 2,000 mg/l, if adequate pH conditions are not maintained [*1*]. As long as the volatile acids are neutralized, higher levels can be effectively treated, after some acclimation, until the soluble cations become inhibitory at concentrations exceeding 4,000 to 7,000 mg/l [*1*].

Heavy metals, while known to be toxic to anaerobic processes by reacting with enzymes to block metabolism, are generally not a concern in anaerobic treatment of pulp and paper effluents, because they precipitate in the presence of sulfide. Iron and nickel, in fact, are two metals that frequently must be added to satisfy micronutrient demands.

Wood extractives (including resin acids) at high concentrations, and organic chelating agents such as DTPA, used for stabilizing hydrogen peroxide in bleaching of mechanical pulps, have been reported to be inhibitory or toxic to anaerobic organism [*13*]. These organic compounds have been detoxified by precipitation with aluminum, iron, and calcium salts [*13*].

In summary, toxicity mitigation can be achieved by several approaches, including removal of toxic constituents from process streams before biological treatment, addition of antagonistic compounds, dilution to nontoxic concentrations, and acclimation of the microorganisms.

ANAEROBIC TREATMENT PROCESS CONFIGURATIONS AND THEIR APPLICATION IN THE PULP AND PAPER INDUSTRY

Five basic anaerobic treatment process configurations and hybrid combinations of these basic configurations have been used successfully to treat various pulp and paper mill effluents in full-scale application or treatability demonstrated in pilot plant studies. These process configurations are:

- Anaerobic Lagoon
- Anaerobic Contact
- Upflow Anaerobic Sludge Blanket
- Anaerobic Biofilter
- Anaerobic Fluidized Bed

TABLE 6. FULL-SCALE ANAEROBIC LAGOON SYSTEMS WITH AEROBIC POLISHING

Mill Name	Inland Container Corporation	Sonoco Products Company
Mill Location	Newport, Indiana	Hartsville, South Carolina
Start-up Date	1979	1987
Wastewater Source	Recycled Paper	Recycled Paper
Anaerobic Volume (mg)	5	24
Influent Flow (mgd)	0.69	4
Retention Time (days)	7.2	6
Temperature	109-118	90-100
BOD_5—Influent (mg/l)	1,898	667-705
—Anaerobic Effluent (mg/l)	297	251-318
—Aerobic Effluent (mg/l)	89	21-24
—Anaerobic Removal (%)	84.4	58.5
—Overall Removal (%)	95.3	96.7
Biogas Production (m^3/kg BOD_5 Removed)	—	0.81
Methane Content (%)	—	65-70
Data Period/Reference Source	Jan. 1980 (30)	Apr./May 1988 (31)

Anaerobic Lagoon

Anaerobic lagoons are the oldest of the engineered anaerobic treatment processes, having been first used in the food processing industry in Australia in the 1940s. An anaerobic lagoon system is schematically depicted in Figure 3.

The influent is initially mixed with inorganic nutrients and micronutrients and is neutralized as necessary to maintain adequate pH conditions in the lagoon reactor. The lagoon is commonly a single cell, but can be configured as multiple cells in series or parallel. The lagoon commonly is of earthen construction and is covered with a synthetic membrane to maintain anoxic conditions, to collect biogas generated from anaerobic degradation of organics, and to control odors. An anaerobic biomass develops in the lagoon and remains partially suspended from mixing induced by the generated biogas. Mixing and contact with the biomass can be enhanced with intermittent use of low-speed mixers and solids recycle. Solids settling, however, is an important feature that can be designed into anaerobic lagoons to provide the time necessary to hydrolyze and degrade particulate material.

Biogas is collected from under the membrane cover normally at multiple points and at a slightly negative pressure to hold the membrane against the water surface. This prevents gas from lifting the cover and forming an airfoil, which in a strong wind can put further lift forces on the cover, causing failure.

While as yet not widely used in the pulp and paper industry, the anaerobic lagoon concept has several advantages over other anaerobic treatment process configurations, including:

- The ability to degrade suspended solids (TSS), since particulate that settles can be held in the reactor for months (or years). Anaerobic lagoons are potentially good applications for high-strength process streams from mechanical and chemical pulping, which also have high fiber content.
- For effluent treatment systems that include activated sludge treatment, waste-activated sludge can be combined with the feed to the anaerobic lagoon for anaerobic digestion of these solids. Thus, the total quantity of biological sludge requiring disposal from a combined anaerobic/aerobic treatment system is reduced.
- Equalization of waste characteristics (organic loading, pH) due to the large volume of the reactor.
- Simplicity of operation.
- Frequently lower capital and operating costs compared to other alternatives.

The primary disadvantages are:

- Large land areas can be required. For most pulp and paper applications, minimum hydraulic retention times of 7 to 10 days would be required to achieve BOD_5 reductions in the range of 75 to 90 percent.
- Heat loss considerations given the large surface area.
- Solids removal from the lagoon may be required at some time, depending upon the quantity of inorganic solids and the degradability of the suspended material in the influent.
- Gas collection from larger surfaces is more difficult.

Inland Container Corporation has had an anaerobic lagoon in operation since 1979 in Newport, Indiana. This treatment facility also has an aerobic polishing step following the anaerobic lagoon. Published operating data for this system are summarized in Table 6. To the authors' knowledge, this is the first full-scale application of any anaerobic technology at a North American pulp or paper mill and perhaps in the world. A similar anaerobic lagoon and aerobic polishing system was installed in 1987 at Sonoco Products Company's recycle and paperboard mill in Hartsville, South Carolina. The first 10 months of oper-

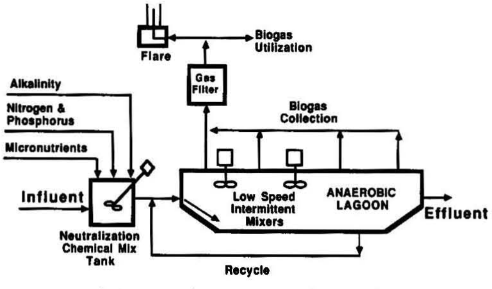

Figure 3. Anaerobic lagoon system schematic diagram.

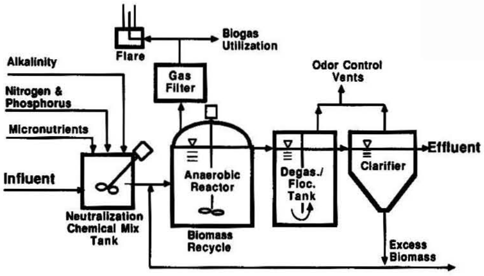

Figure 4. Anaerobic contact system schematic diagram.

Table 7. Full-Scale Anaerobic Contact Process Facilities

									Performance				
			Design Influent Condition						Removals				
Mill Location	Wastewater Source	Start-Up Date	Flow (mgd)	BOD_5 (mg/l)	COD (mg/l)	TSS (mg/l)	S (mg/l)	Reactor Loading Rate (kg COD/m^3/d)	BOD (%)	COD (%)	Gas Production (m^3/d)	CH_4 Content (%)	Reference
Hylte Bruks AB, Sweden	TMP, Groundwood Magnetic, Deink	1983	2.3	1,300	3,500	520	—	2.5	71	67	7,500	60-70	(33)
SAICA Zaragoza, Spain	Wastepaper Akaline Cooked Straw	1984	1.3	10,000	30,000	—	—	4.8	94	66	40,800	70-75	(33)
MoDo Cell AB Domsjo, Sweden	Sulfite Condensate, CTMP	1984	3.4	4,000	10,000	—	700	4.3	95	65	50,400	55-90	(33)
Hannover Paper Alfred, Germany	Sulfite Condensate	1984	0.4	3,000	6,000	—	50	4.2	97	85	2,900	70-90	(14)
Niagara Of Wisconsin Wisconsin	Groundwood	1986	1.4	2,500	4,800	3,300	—	2.7	96	77	—	—	(6)
SCA Ostrand Ostrand, Sweden	CTMP	1987	1.0	3,700	7,900	—	—	6.0	50	40	4,000*	—	(33)
E. Holtzmann & Cia AG Kartrube, Germany	Sulfite Condensate	1988[1]	1.0	4,000	6,400	—	—	4.0	—	—	8,100[2]	70-80[2]	(33)
Modern Kartoon Istanbul, Turkey	Wastepaper, Alkali Wheatstraw	1988[1]	0.7	7,000	20,000	—	—	—	—	—	—	—	(33)
Alaska Pulp Corporation Sitka, Alaska	Sulfite Condensate, Bleach Caustic Extract, Pulp Whitewater	1988[1]	4.3	3,500	10,000	—	—	3.0	85[2]	49[2]	20,100[2]	65[2]	(33)

*Methane yield

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[1] Under construction
[2] Expected performance
—No data available.

ating data indicate that performance is continuing to improve and that equilibrium conditions have not been attained. Average performance for the last 2 months reported are included in Table 6. These are the only full-scale anaerobic lagoon systems operating in the pulp and paper industry of which the authors are aware.

On a pilot scale, ADI International, Fredericton, New Brunswick, Canada, has demonstrated low-rate anaerobic lagoon treatability of a variety of paper mill effluents, including kraft and sulfite evaporator condensates, soda and neutral sulfite semi-chemical spent liquor, acid sulfite spent liquor, bleachery effluents, boardmill effluent, and paper mill whitewaters [*32*].

Anaerobic Contact

The anaerobic contact process is an outgrowth of the anaerobic lagoon. To reduce reactor volume, the biomass concentration is increased by separating and returning solids from the effluent. In this respect, the anaerobic contact process is very similar to activated sludge.

Figure 4 is a schematic diagram of the process. After chemical addition to provide essential nutrients, and neutralization if needed for pH control, the influent and biomass are brought into intimate contact in a completely mixed reactor. Efficient mixing and solids separation are critical to successful process operation. Mixing induced by biogas generation is usually supplemented by side-mounted or top-entering low-speed mechanical mixers or mechanically recirculated biogas. A positive pressure (normally 15 to 20 inches H_2O) in the reactor results in supersaturation of dissolved gases in the effluent. Degassing and reflocculation of the biomass are essential for efficient gravity separation.

Because of the low cell yield inherent to anaerobic metabolism, solids separation is the Achilles heel of this process, and efficient separation becomes increasingly more critical with reduction in waste strength. Both conventional gravity and lamella plate separators have been successfully used for effluent solids separation. The shorter hydraulic residence time of the lamellas minimizes the adverse effects of gas generation from continued anaerobic activity, while conventional clarifiers afford a better opportunity for solids thickening and maintenance of higher biomass concentration in the reactor.

The anaerobic contact process was the first attempt at a high-rate process in the United States, with startup of a system at a meat packing plant in Albert Lea, Minnesota, in 1959 [*1*]. The Swedish Sugar Company developed anaerobic contact technology in the late 1960s and early 1970s to treat wastewaters from their beet sugar plants. This technology was sold to other industries, and with startup of an anaerobic contact system at Hylte Bruks, Sweden, in 1983, it became the first high-rate anaerobic process used in the pulp and paper industry [*3*]. An anaerobic contact system designed by CH2M HILL for a groundwood and coated paper mill in Niagara, Wisconsin, and placed into operation in 1986, was the first high-rate anaerobic treatment facility to be used in North America.

There are currently at least seven full-scale anaerobic contact systems in operation at pulp and paper mills worldwide, and at least three more are under construction. Table 7 summarizes the location, type of mill, waste characteristics, and actual or anticipated performance.

Purac AB, a Swedish company, now licenses the technology developed by the Swedish Sugar Company. Infilco Degremont, Inc., a worldwide supplier of water and wastewater treatment equipment, also currently has licensed anaerobic contact technology operating in the pulp and paper industry.

Because suspended solids in the feed as well as biosolids produced from anaerobic metabolism of soluble organics are separated from the effluent and returned to the reactor, the anaerobic contact process can provide the sludge age necessary for hydrolysis of degradable organic particulate material. This is one advantage of anaerobic contact over other high-rate anaerobic processes, that makes it particularly well-suited to pulp and paper mill effluents with relatively high TSS concentrations, such as mechanical pulping whitewaters. In other high-rate anaerobic processes, including the UASB, anaerobic filter, and anaerobic fluid bed, biomass produced from degradation of soluble substrate is held in the reactor principally as dense granules or biofilms on an inert medium. The retention time of influent suspended particulate is normally not much longer than the reactor hydraulic residence time and generally is too short for hydrolysis of the cellulosic fibrous material from wood pulping.

Reactor volatile solids concentrations reported for anaerobic contact systems operating in the pulp and paper industry have ranged from 3,000 to 5,000 mg/l [*6*] to over 10,000 mg/l [*14*], resulting in volumetric loadings in the range of 1 to 2 kg BOD_5 removed/m^{3}d at BOD_5 removal efficiencies greater than 90 percent and at optimum temperatures of 35 ± 5 degrees C. These volumetric loading rates are perhaps 20 to 50 percent of those that can be achieved by other high-rate anaerobic treatment configurations. Thus, anaerobic contact may be at some disadvantage compared with other high-rate systems where onsite space is limited.

Upflow Anaerobic Sludge Blanket (UASB)

Development of the UASB process in the 1970s by Lettinga and co-workers at the University for Agriculture at Wageningen in the Netherlands was a major advance in high-rate anaerobic treatment technology [*34*]. In an upflow reactor, anaerobic bacteria form dense granules that settle and remain in a bed at the bottom of the reactor. The suspended solids concentration of the sludge bed is commonly 8 to 13 percent dry solids, with a volatile content of 60 to 90 percent.

The UASB is schematically described in Figure 5. After chemical addition to provide nutrients and neutralization as needed, the influent is distributed over the bottom of the reactor to maintain even flow distribution in the sludge bed, typically 1 to 2 meters (3 to 6 feet) deep. Mixing of the bed to bring the granules into contact with the soluble organics is achieved by hydraulic flow distribution and turbulence resulting from biogas generation.

Above the bed, a more flocculant sludge blanket forms, typically 3,000 to 10,000 mg/l dry solids in consistency. At

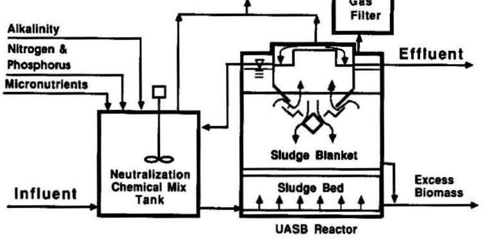

Figure 5. Upflow anaerobic sludge blanket (UASB) schematic diagram.

Table 8. Full-Scale Upflow Anaerobic Sludge Blanket (UASB) Facilities

Mill and Location	Wastewater Source	Start-Up Date	Design Influent Condition: Flow (mgd)	Design Influent Condition: BOD_5 (mg/l)	Design Influent Condition: COD (mg/l)	Design Influent Condition: TSS (mg/l)	Reactor Loading Rate (kg COD/m^3/d)	Performance: Removals: BOD (%)	Performance: Removals: COD (%)	Performance: Gas Production (m^3/hr)	Performance: CH_4 Content (%)	Reference
Ceres, Holland	Boxboard	1983	0.03	3,150	6,300	—	9	85	70	—	—	(36)
Roermond, Holland	Corrugating	1983	0.9	2,250	4,500	—	20	85	75	—	—	(36)
Celtona, Holland	Tissue	1984	0.8	600	1,200	—	5	75	60	—	—	(36)
Industriewater, Holland	Corrugating, Boxboard	1985	3.2	550	1,100	—	6	80	70	—	—	(36)
Davidson, United Kingdom	Linerboard	1986	1.3	1,440	2,880		9	90	75	—	—	(36)
Mayr McInhof, Austria	Folding Box Board	1987	1.6	1,200	2,500	—	10	75	65	—	—	(36)
Emin Leydier, France	Corrugating	1987	0.6	1,700	3,550	—	8.5	85	75	—	—	(36)
Tillman, West Germany	Corrugating	1987	0.4	7,500	15,000	—	15	90	80	—	—	(36)
Italcarta, Italy	Corrugating	1988[1]	1.7	1,250	2,500	—	8.5	85[2]	70[2]	—	—	(36)
APPM, Australia	Fine Paper	1988[1]	0.06	1,500	4,000	—	7	90[2]	75[2]	—	—	(36)
Quesnel River Pulp British Columbia, Canada	TMP/CTMP	1988[1]	2.1	3,000	7,000	—	19	50[2]	35[2]	—	—	(36)
Lake Utopia Paper New Brunswick, Canada	NSSC	1988[1]	1.0	6,000	16,000	—	20	80[2]	50[2]	—	—	(36)
P.W.A. Redenfelder West Germany	Wastepaper	1988[1]	0.95	—	2,800	—	10	90[2]	75[2]	156[2]	70[2]	(37)
Consolidated Bathurst Bathurst, New Brunswick	NSSC/CTMP	1988[1]	4.1	—	12,000	333	11.9	85[2]	60[2]	2,080[2]	70[2]	(37)
MacMillan Bloedel Ontario, Canada	NSSC/TMP	1989[1]	1.8	8,300	25,000	—	18.5	75[2]	50[2]	—	—	(36)

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[1] Under construction
[2] Expected performance
—No data available

the top of the reactor, a three-phase separator is necessary to separate the biogas and entrained solids from the liquid. The design of these integral gas/liquid/solids separators varies among suppliers of UASB technology. A recycle flow is normally used to maintain a constant hydraulic loading on the reactor and to dilute influent waste as needed.

The UASB has several advantages compared with other high-rate anaerobic systems. If the reactor is seeded with adapted granular sludge from another full-scale plant treating a similar waste, start-up can be very rapid. Depending on the quantity of biosolids and acclimation to the waste, start-up time can be as short as a few days. Reactors seeded with granular sludge equivalent to 10 to 15 percent of the design biomass typically achieve full load operation within 3 to 6 weeks from initial start-up. Start-up of anaerobic contact and anaerobic filters may take 3 months or longer to reach full load capability, and anaerobic lagoons can take up to 1 year.

Because of the dense nature and consequent settleability of the granular sludge, the washout rate of biosolids in a UASB can be very low. For this reason, the UASB process can anaerobically treat much lower waste strengths than those normally considered feasible—as low as 400 mg/l BOD_5 [*17*]. The ability of the high biomass concentration in the reactor to withstand organic or toxic shock loads with minimum adverse effect on performance, as well as with no requirement for mechanical mixing in the reactor, are also advantageous features of the UASB.

Granulation of the sludge is the most critical factor in UASB performance. If the wastewater characteristics are such that granules will not form or that granulation is lost due to toxicity or some other condition adversely affecting growth of the sludge bed, the biomass will be lost, and system performance will be severely hampered. High concentrations of influent TSS also can have an adverse effect on the performance of the sludge bed. This is particularly a problem if biogas production is not adequate to keep the bed sufficiently mixed to allow suspended material to pass through the bed. In general, the suspended solids content of the feed should not exceed 10 percent of the total COD concentration [*35*].

With commercialization in the late 1970s and early 1980s, the UASB has been used increasingly in a wide variety of industries, including pulp and paper. Since start-up in 1983 of the first full-scale systems at Ceres and Roermond Papier, wastepaper recycle mills in the Netherlands, there are currently at least eight UASB treatment facilities operating worldwide and another seven under construction or in start-up, four of which are in Canada. The location, type of mill, waste characteristics, and actual or design performance are summarized in Table 8. Loading rates for these installations are typically in the range of 3.5 to 5.0 kg BOD_5 removed/m^3/day at optimum operating temperatures of 35 ± 5 degrees C.

UASB technology is offered by several suppliers including: Paques B. V., the Netherlands, and their North American licensee, Paques Lavalin; Gist Brocades, the Netherlands, and their North American licensee, Biothane Corporation; and Biotim N. V., Belgium, and their North American licensee, Lotepro.

Anaerobic Filter

Although considerable anaerobic filter research was conducted in the 1960s, the first large-scale commercial facilities using high-void volume synthetic media were not built until 1977, when Celanese Corporation constructed the first of three systems at Vernon, Texas, to treat petrochemical plant wastewaters [*1*]. Bacardi Corporation installed a very large (9,200 m^3) anaerobic filter in San Juan, Puerto Rico, which has been in continuous, successful operation since 1981. To the authors' knowledge, the first full-scale anaerobic filter for treating pulp and paper effluent was only recently constructed in 1987 at an integrated mill with CTMP pulping in Lanaken, Belgium, but it has not been started up because of modifications to the pulp mill. Although treatment performance and successful operation have been demonstrated in other industries, particularly the Bacardi facility, the lack of acceptance of the anaerobic filter configuration by the pulp and paper industry may be related to filter media cost and possibly a concern for potential plugging of the media, which did occur in the Celanese facilities after a few years of operation.

The anaerobic filter concept is schematically shown in Figure 6. Fixed media in the reactor provides support for development of high concentrations of active biomass. Attachment to a fixed surface minimizes or virtually eliminates the risk for washout of the biomass. The biomass film thickness and total quantity in the reactor are influenced largely by process configuration and characteristics of the support media.

Anaerobic filters can be operated in an upflow and in a downflow mode. The original Celanese units were upflow. The principal advantage of the upflow mode is that higher biomass concentrations can be developed, because in addition to formation of a biofilm, suspended biomass becomes entrapped in the structure of the fixed bed media. Entrapment of biosolids in the upflow mode can result in faster start-up and greater overall volumetric loading than downflow operation.

Entrapment of solids, whether biologically produced or that contained in the influent, is also the major drawback of the upflow anaerobic reactor, leading to media plugging and hydraulic short-circuiting. Even flow distribution is also more difficult to achieve with upflow reactors.

The downflow design largely solves the plugging problem, as biomass is mainly in the form of biofilm. The Bacardi system has been operating for more than 7 years at influent TSS concentrations of up to 8,000 mg/l without evidence of plugging [*38*]. Flow distribution in the manner of a rotating arm, much like a trickling filter, is much simpler in the downflow mode.

The downflow mode has one other unique advantage over the other high-rate anaerobic configurations, including the upflow anaerobic filter, that can be particularly applicable to treatment of pulp and paper mill effluents with a high inorganic sulfur content and a low (less than 10 to 15) degradable COD to inorganic sulfur ratio. Downflow operation, in effect, allows for physical separation of the faster-growing, sulfur-reducing bacteria in the upper portion of the reactor fixed media from the slower-

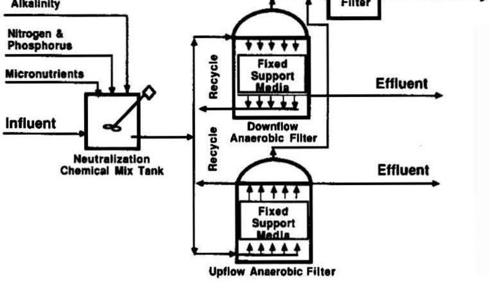

Figure 6. Upflow and downflow anaerobic filter schematic diagram.

TABLE 9. FULL-SCALE ANAEROBIC FILTER FACILITIES

Facility	KNPC	Barcardi Corporation
Location	Lanaken, Belgium	San Juan, Puerto Rico
Start-up Date	1988**	1981
Wastewater Source	CTMP	Run Distillery
Influent Conditions		
—Flow (mg/l)	1.3*	0.4
—BOD_5 (mg/l)	4,000*	31,500
—COD (mg/l)	7,900*	75,000
—TSS (mg/l)	—	3,000-8,000*
—Sulfur-as S (mg/l)	—	1,300-3,300*
Reactor Loading (kg COD/m^3/d)	12.7*	12.8
Removal—COD (%)	70*	50
—BOD_5 (%)	85*	71
Biogas Production (m^3/hr)	443*	1,590
Methane Content (%)	85*	66

*Design conditions.

**Anaerobic filter system construction completed 1987, awaiting CTMP mill startup.

growing methanogenic bacteria in the lower layers. The biogas produced in the lower levels of the reactor tends to strip out the hydrogen sulfide, protecting the toxicity-sensitive, methane-forming bacteria. Thus, the downflow anaerobic filter can, in effect, function as a two-stage reactor, and should be able to tolerate much higher inorganic sulfur levels at lower degradable COD to inorganic sulfur ratios than other single-stage anaerobic reactors.

Recycle is an essential feature that must be incorporated in both upflow and downflow anaerobic filters, to minimize pH gradients through the reactor bed, to maintain hydraulic conditions that assure good flow distribution and minimize short-circuiting, and to minimize toxicity effects due to concentration.

The severity of a toxic condition in biological treatment systems depends on concentration, exposure time, and adaptation. Biomass can generally stand short duration exposure at high concentrations better than longer term exposure at low concentration. Attached biofilm systems such as anaerobic filters and fluidized beds, therefore, are much more resistant to shock loads than suspended growth processes such as anaerobic contact.

Design performance data anticipated for the KNPC facility in Lanaken, Belgium, are summarized in Table 9. Because the effluent produced from fermentation of molasses is, in many respects, similar to some pulp and paper wastes (5-carbon sugars, organic acids, and low molecular weight alcohols), data from the Bacardi system have also been included in Table 9.

The higher biomass density of the fixed film anaerobic filters has allowed volumetric loadings of 4 to 15 kg BOD removed/m^3-day to be achieved in pilot studies on pulp and paper mill wastewaters as well as in full-scale application in other industries [39] [*40*].

Licensed anaerobic filter technology is available from a number of suppliers including Bacardi Corporation, Badger (the Celanese-developed technology), and Infilco Degremont.

Anaerobic Fluidized Bed

The anaerobic fluidized bed is also a fixed film process in which a biofilm is allowed to grow on sand particles or other inert media that are hydraulically held in suspension. Bench and pilot scale studies of the anaerobic fluidized bed have demonstrated its technical viability for efficient treatment of a variety of industrial effluents, including pulp and paper mill wastewaters [*40*].

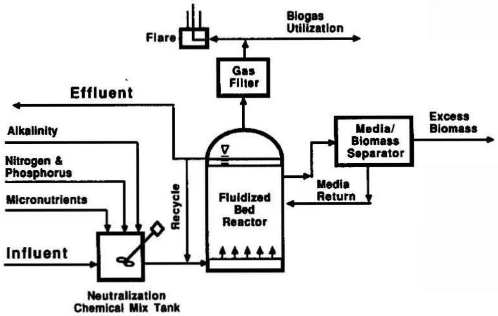

Figure 7. Anaerobic fluidized bed reactor schematic diagram.

The anaerobic fluidized bed process is schematically shown in Figure 7. Following chemical addition for inorganic nutrient and pH control, flow is evenly distributed in the bottom of the reactor at an upflow velocity sufficient to fluidize the bed. Recycle about the reactor is used to maintain this constant upflow velocity condition as well as to minimize pH gradients and toxic or inhibitory conditions due to concentration. The reactor bed will continue to expand as the biofilm grows on the surface of the media and as soluble organics are metabolized. To control bed expansion and the quantity of biosolids in the reactor, media is withdrawn periodically when the bed reaches a predetermined height and passes through a media/biomass separation device, such as an inclined wedge wire static screen. Biosolids separated from the media are wasted, and the clean media is returned to the reactor.

Bench and pilot studies have demonstrated that the anaerobic fluid bed can achieve the highest volumetric loadings of the high-rate anaerobic process configurations discussed, while maintaining similar treatment efficiencies. In a pilot study treating evaporator condensate from an ammonia-based sulfite mill, an anaerobic filter, a UASB, and an anaerobic fluidized bed reactor were operated side by side [*40*]. Each reactor configuration had similar BOD_5 removal efficiencies of 80 to 90 percent, but the fluidized bed was able to operate at volumetric loadings of 17 to 41 kg BOD_5 removed/m^3/day compared to 3.0 to 3.3 kg BOD_5 removed/m^3/day for the UASB, and about 10 kg BOD_5 removed/m^3/day for the anaerobic filter.

Following a year of pilot studies at a paperboard mill in D'Aubigne Racan, France, a full-scale anaerobic fluidized bed system is now under construction and scheduled for start-up toward the end of 1988. The design performance expected from this system, is summarized in Table 10.

TABLE 10. FULL-SCALE ANAEROBIC FLUIDIZED BED FACILITIES

Facility	Allard Paper Company
Location	D'Aubigne Racan, France
Anticipated Startup	Late 1988
Wastewater Source	Paperboard
Influent Conditions	
—Flow (mg/d)	0.40
—COD (mg/l)	3,000
—BOD_5 (mg/l)	1,500
Reactor Loading (kg COD/m^3/d)	35
Removals—COD (%)	72.2
—BOD_5 (%)	83.3
Effluent TSS (mg/l)	53
Biogas Production (m^3/hr)	75
Methane Content (%)	65

The ability to operate at very high volumetric loadings with high removal efficiencies, and consequently a smaller reactor volume, is a significant advantage of the anaerobic fluidized bed process. Where space is very limited, the anaerobic fluid bed may have a significant advantage over other high-rate anaerobic processes. Its principal disadvantages have been higher power requirements and consequently higher operating costs, perceived (if not actual) increased complexity and operator skill level required, and higher overall capital cost.

Suppliers of licensed anaerobic fluidized bed technology include Infilco Degremont, Air Products and Chemicals (previously developed by Dorr Oliver), and Gist Brocades.

Hybrid and Two-Stage Anaerobic Configurations

A number of hybrid reactor configurations combining two or more anaerobic process configurations such as the UASB/fixed media system schematically described in Figure 8 have been developed and evaluated in pilot plants or at full scale. Hybrid systems are designed to take advantage of unique features of two or more process concepts. As an example, where adapted granular sludge is not available, the UASB/fixed film hybrid may offer a faster start-up than UASB alone. Development and entrapment of a flocculant anaerobic biomass, as well as growth of a fixed biofilm, normally proceed more rapidly than development and growth of granular sludge from an initial flocculant seed.

Other potentially advantageous features of the UASB/fixed film hybrid anaerobic reactor include:

- Higher overall reactor biomass concentrations than UASB alone, resulting in a smaller reactor volume.
- Greater resistance to toxicity shock loads by having both a granular and a fixed film biomass.
- Where biofilm support media cost is high, the combination of processes may offer a capital cost advantage over an anaerobic filter alone, sized to achieve a similar treatment efficiency.

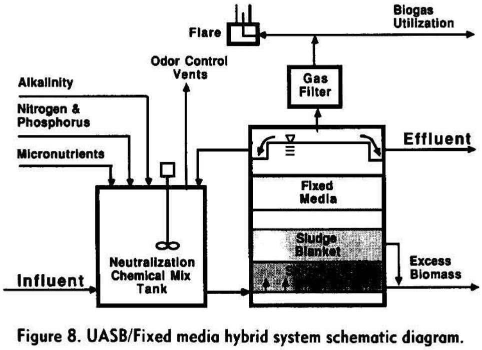

Figure 8. UASB/Fixed media hybrid system schematic diagram.

The primary disadvantage may be eventual plugging of the fixed media operating in an upflow mode and the potential difficulty of optimizing two processes physically housed in a single vessel for a wide range of flow and loading conditions.

At least two hybrid systems have been installed at pulp and paper mills in Finland and New Zealand. Both of these facilities are two-stage systems where the acidogenic and methanogenic stages are physically separated into sequential reactors. The TAMAN process, developed by Tampella, was piloted in the early 1980s, and a full-scale system was constructed in 1985 at the Anjala Paper Mill (Anjalinkoski, Finland) to treat mechanical pulping and debarking plant effluents. Little information or operating data from the combined fixed growth packed bed and sludge bed process have been released for publication.

Caxton Paper Mills, Ltd., Kawerau, New Zealand, has installed a two-stage anaerobic system in conjunction with construction of a new CTMP mill. The methane-producing second stage combines the UASB process with highly porous polyurethane foam, a carrier material developed by Biotim N. V., the Netherlands. The combined UASB/Polyurethane Carrier Reactor (PRC) is designed to provide a fast start-up where granular sludge is not available and to provide high reactor stability with a wastewater known to be difficult to treat. Construction-related problems have delayed the start-up of this plant until 1989.

Separation of the acid-forming and methane-forming phases into two stages, at least in theory, allows the design and operation of each phase to be optimized independently of the other. The hardier facultative acid-forming bacteria in the first stage can provide significant protection to the more sensitive methanogenic strict anaerobes. This is particularly the case when oxidants such as hydrogen peroxide are present in the wastewater. Both Anjala Paper Mill and Caxton Paper Mills bleach mechanical pulp with hydrogen peroxide.

Inorganic Sulfur Removal

Inorganic sulfur, a constituent of many pulp and paper mill effluents, can affect the viability of anaerobic treatment. While sulfur is an essential nutrient that is required by anaerobic bacteria, inorganic sulfur levels that result in a degradable COD-to-sulfur ratio of less than about 10 to 15:1 at neutral pH conditions are likely to result in hydrogen sulfide toxicity. Four methods have been used to mitigate potential hydrogen sulfide toxicity to anaerobic treatment systems at pulp and paper mills:

- Removal of sulfur from the feed
- Metal precipitation of sulfide
- Hydrogen sulfide stripping and reactor biogas recirculation
- Two-stage anaerobic treatment in which sulfur is reduced to hydrogen sulfide and removed in the first stage.

Condensates that contain sulfur dioxide can be effectively steam-stripped to remove sulfur. Hannover Papier is able to reduce the SO_2 content from 1,500 to between 10 and 30 mg/l [*14*]. This is sufficient to reduce the total sulfur content to less than 100 mg/l (as S), thus maintaining degradable COD at a ratio greater than 30:1.

Heavy metals will precipitate sulfides to very low solubilities. Precipitation with iron salts has been used effec-

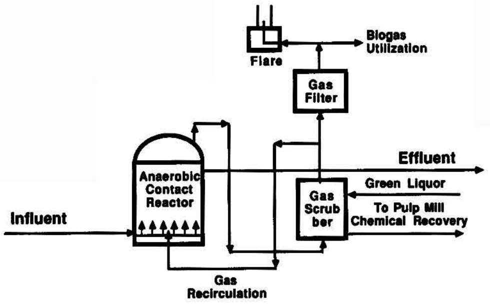

Figure 9. H_2S removal by gas scrubbing and recirculation in an anaerobic contact reactor.

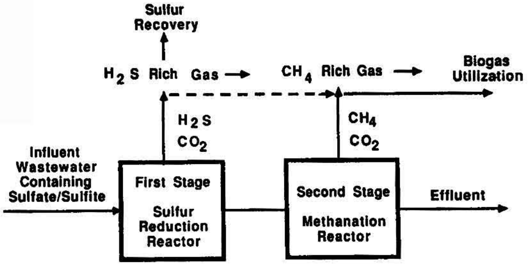

Figure 10. Conceptual diagram for two-stage anaerobic treatment systems with sulfur removal.

tively where hydrogen sulfide levels in the reactor have been marginally inhibitory. The major drawback with this method of hydrogen sulfide removal is the cost of iron salts. The precipitated iron will also reduce the volatile content of the biomass (which may or may not be a consideration), increase total sludge production, and limit the alternatives to dispose of waste sludge where total heavy metal content is a concern.

Scrubbing hydrogen sulfide from the biogas and recirculating part of the stripped biogas to the reactor is used by at least one mill to control hydrogen sulfide. MoDoCell AB, Ornskoldsvik, Sweden, circulates biogas from two large anaerobic contact reactors through a counter current scrubbing tower in which green liquor, containing sodium sulfide and sodium carbonate is used to absorb hydrogen sulfide as shown on Figure 9. Carbon dioxide is also absorbed, which requires additional alkalinity. This is not an added operating cost at this mill, however, because both hydrogen sulfide and carbon dioxide are used in the pulping liquor chemical recovery process.

Separation of the sequential anaerobic process into two stages (Figure 10) has been used effectively by Junckers Industrier A/S, Kige, Denmark, to remove hydrogen sulfide prior to the methane formation stage [*41*]. The first stage is an anaerobic trickling filter. The feed cascades down the fixed media on which a biofilm of sulfate-reducing bacteria has developed. The ANTRIC (ANerobic TRICkling Filter) was developed by PURAC (formerly A.C. Biotechnics), and patents have been applied for.

The two-stage Biotim anaerobic system at Caxton Paper Mills was designed to remove hydrogen sulfide in a similar manner. The first stage can be operated as either a contact reactor with biogas stripping or as a UASB.

Sulfur can be recovered from a hydrogen sulfide-rich biogas stream as elemental sulfur through an oxidation-reduction process, using iron or nickel as a regenerative carrier or catalyst. This system is schematically shown in Figure 11, and has been used commercially in Northern California to remove and recover sulfur from geothermal power generation plants.

CONCLUSIONS

Application of anaerobic treatment is rapidly gaining acceptance in the pulp and paper industry. Since 1983, with successful start-up and operation of the first high-rate systems, at least 16 full-scale anaerobic treatment facilities are currently in operation worldwide, and another nine are either in start-up or are under construction.

The characteristics of many of the process effluents from pulp and paper mill operations are well suited for degradation by anaerobic processes. These wastestreams are warm and contain low molecular weight organic acids, alcohols, and sugars that are readily metabolized to methane by anerobic bacteria.

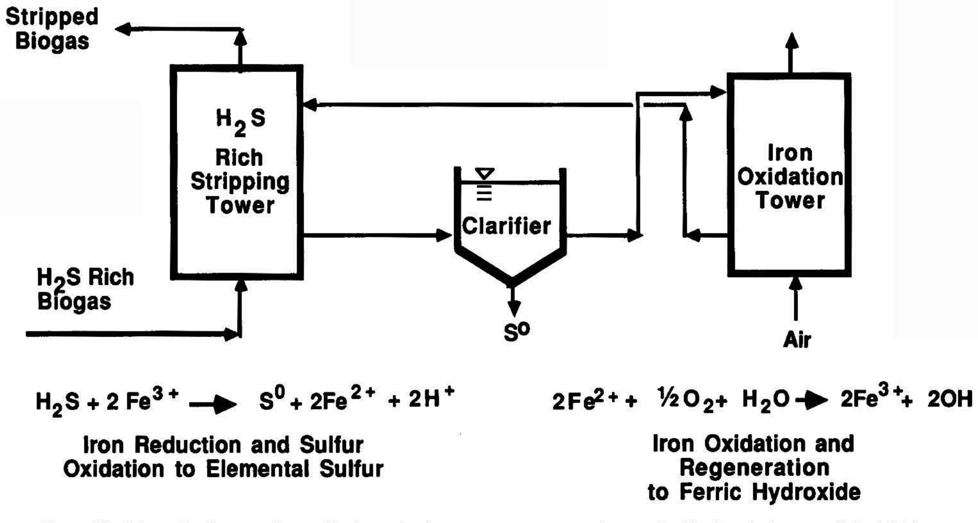

Figure 11. Schematic diagram of an oxidation-reduction process to recover elemental sulfur from hydrogen sulfide-rich biogas.

Inorganic sulfur, wood extractives, and certain organic and inorganic additives can produce inhibitory or toxic conditions that must be dealt with in the design and operation of an anaerobic treatment facility.

Several anaerobic process configurations have been successfully applied to treatment of pulp and paper mill wastewaters, including: anaerobic lagoon, anaerobic contact, UASB, anaerobic filter, anaerobic fluidized bed, and hybrids of two or more of these basic configurations. No single process is best for all applications. Each configuration has unique advantages as well as tradeoffs, compared with other anaerobic processes. Treatment objectives, waste characteristics, and site-specific factors will influence which systems are technically and economically the most attractive for each application.

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Waste Minimization Opportunities At An Electric Arc Furnace Steel Plant Producing Specialty Steels

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Waste reduction assessments have been carried out in the Armco, Inc. Butler, Pennsylvania electric arc furnace (EAF) specialty steelmaking complex. These assessments were intended to develop waste reduction options for two hazardous waste streams at this facility: heavy metals waste and corrosive waste. Waste reduction options considered were in one of two categories: source reduction or recycling (in the same order of preference). Treatment was considered only if waste reduction options were unavailable.

INTRODUCTION

Following the Congressional mandate on reduction of hazardous waste as expressed in the Hazardous Solid Waste Amendments of 1984 (HSWA), the EPA Office of Research and Development Hazardous Waste Engineering Research Laboratory (HWERL) during 1986 and 1987 offered various industrial facilities the opportunity to act as host sites at which specially selected group of engineering consultants (under EPA sponsorship) would assess the opportunities for reduction of selected hazardous wastes generated at these sites. One of the industrial facilities agreeing to act as a host site for a waste reduction assessment was the Armco Inc. Specialty Steel Division in Butler, Pennsylvania. Versar Inc. was selected by EPA to be the engineering consultant to perform the assessment. The results of the assessment conducted at the Armco facility are discussed in this paper.

In the course of performing the waste reduction assessments, the consultants involved were to apply and refine as appropriate a methodology developed for carrying out these assessments. The methodology as finally developed is described in detail in "The EPA Manual for Waste Minimization Opportunity Assessments" [*1*].

DEVELOPMENT OF WASTE REDUCTION OPPORTUNITIES

The primary emphasis in this waste reduction assessment was to develop and evaluate waste reduction opportunities for two principal hazardous wastes generated at the Armco Inc. facility: emission control dust and sludge from electric arc furnace (EAF) steelmaking operation; and waste pickle liquors and rinse waters from cleaning of the stainless and alloy steel strip products prior to shipment. This assessment was performed during the summer of 1986. The Versar assessment team included the assessment project manager (a senior chemical engineer with 37 years of process engineering and project management experience including approximately 13 years of environmental engineering experience), a senior physical chemist with 20 years of experience, and a steel industry consultant (a metallurgical engineer with 40 years of experience). The assessment focused on two plant areas that generate these wastes: the melt shop in the main plant where the EAF emission control waste is generated, and plant no. 2, which generates a hydrofluoric acid/nitric acid pickle liquor and rinsewater from cleaning of stainless steel strip prior to shipment. Other pickling facilities in the main plant generate a number of sulfuric acid, hydrofluoric acid, and nitric acid wastewater streams, but these wastes are presently comingled prior to wastewater treatment. Plant No. 2 generates a single segregated pickle liquor waste stream that appeared amenable to waste reduction possibilities. Each of the assessments performed at the two Armco facilities are described below.

Melt Shop Emission Control Sludge Waste Reduction Assessment

Based on the facility information received by the assessment team, process and waste handling operations at Armco's main plant were as follows. The main plant at Armco's facility consists of three electric arc furnaces (EAFs) in the melt shop that produce stainless and silicon steels, hot and cold rolling operations to fabricate steel strip and coil, six pickling lines for both stainless and silicon steels, and annealing facilities located in several buildings on a site covering about one square mile. Also located on the site are wastewater treatment facilities, the engineering services building, and a number of surface impoundments used for disposal of nonhazardous liquids and sludges generated primarily from on-site neutralization of spent pickling liquors and rinse waters. The facility produces several types of silicon steels as well as 300 and 400 series stainless steels. Since 1987, the facility also produces a significant quantity of low carbon mild steel. However, plant management is currently planning on returning to the stainless/alloy steel production regime.

Silicon and stainless steels (the latter made in 300 and 400 series) are produced by melting selected batches of scrap, fluxes (including fluorspar), and ferroalloy additives in the presence of oxygen in three-165 tons EAFs at

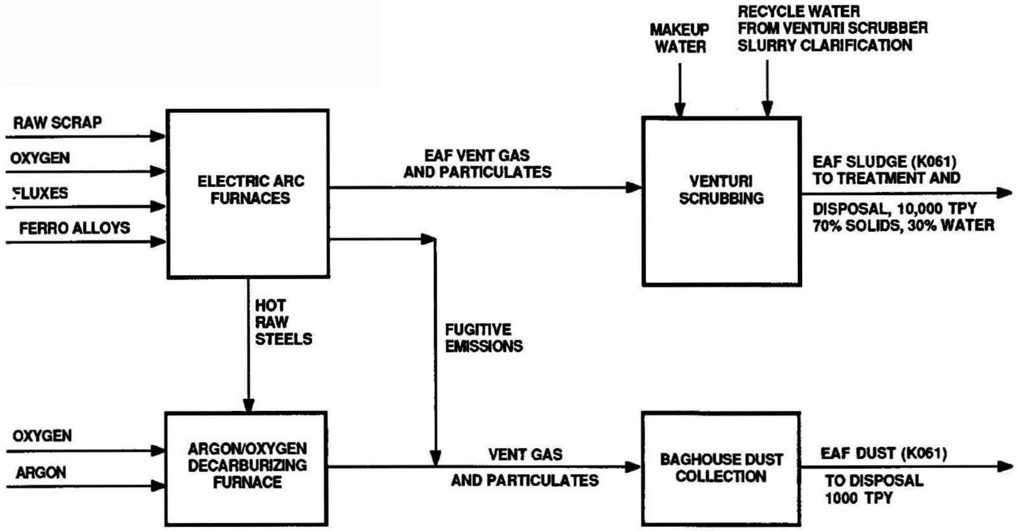

Figure 1. Simplified schematic of K061 waste generation and treatment at Melt Shop, Armco, Inc., Butler, PA.

the melt shop. Approximately 670,000 tons of EAF steels are produced annually at the Butler, facility. The three EAFs, together with an AOD furnace at the melt shop, generate vent gases containing about 8,000 tons per year (TPY) of particulate emissions. Of these emissions, approximately 7,000 TPY are removed from the EAF vent gases using venturi scrubbing; the remaining 1,000 TPY are recovered as EAF fugitive emissions as well as from AOD vent gases using a reverse-air baghouse. Figure 1 is a simplified schematic of the K061 waste generation and treatment processes.

Assessment Step

This phase of this waste reduction assessment began with a detailed inspection of the melt shop area by the Versar team. During this visit, the processes that generate and treat the K061 waste were carefully studied. The process flow was traced from the point of waste generation to the discharge of the treated K061 waste. A schematic illustrating the existing waste treatment procedure is shown in Figure 2.

The melt shop generates EAF emission control dust and sludge. Table 1 is the most recent metals analysis of the EAF venturi scrubber sludge available from the plant; the data shown were obtained in 1983. The venturi sludge represents about 90% of the K061 hazardous waste discharge from the plant. Also included in Table 1 is a recent Versar analysis (1987) of the baghouse dust representing AOD and fugitive emissions from the melt shop.

As shown in Figure 2, the present EAF dust treatment process consists of a water clarification system for the venturi scrubber slurry (the latter contains about 10,000 ppm solids as produced in the venturi scrubber) and a system for treating a blowdown stream of recycled water from the venturi scrubber slurry clarification step (about 10% of the venturi scrubber flow) for hexavalent chro-

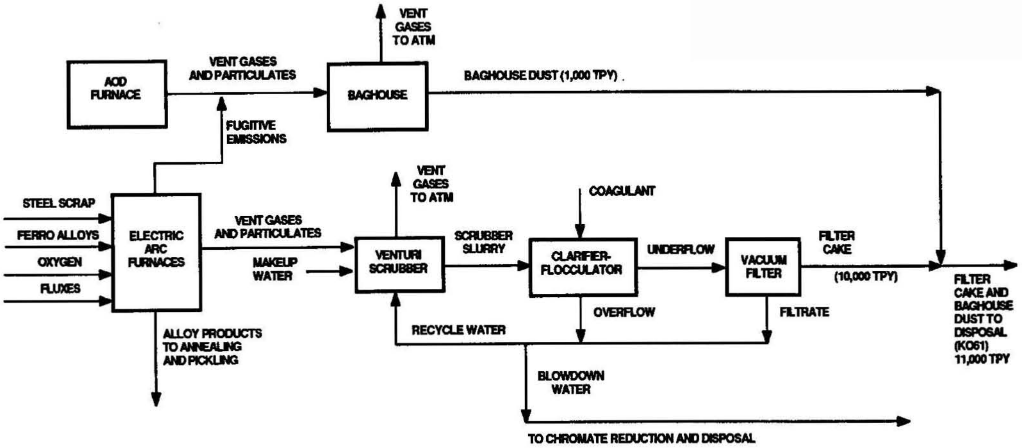

Figure 2. Simplified schematic of EAF dust treatment at the Armco Main Plant, Butler, PA.

TABLE 1. COMPOSITION OF ARMCO MELT SHOP EAF EMISSIONS CONTROL WASTE (K061).

Parameter	Amount present (weight percent, dry basis) Venturi sludge[a]	 Baghouse dust[b]
Iron	39.9	27.6
Manganese	3.4	2.8
Silica (SiO_2)	4.9	—
Aluminum	0.3	0.3
Calcium	3.1	5.8
Chromium (total)	1.7	1.2
Copper	0.25	1.7
Nickel	0.36	0.69
Lead	3.1	0.73
Zinc	10.5	8.4
Magnesium	2.3	3.1
Cadmium	0.041	0.009
Barium	0.011	0.002

[a] Armco data (1983).
[b] Versar data (1987).

mium reduction (the latter system not shown). The clarifier underflow sludge from the water clarification system is filtered in a rotary vacuum filter. The filter cake is then combined with the baghouse dust collected from the decarburizing operation and melt shop fugitive emissions, and the total waste stream (11,000 TPY) classified as K061 is sent to offsite hazardous waste landfills. Armco's disposal cost is $100/ton or approximately $1,000,000 per year to dispose of the K061 waste.

Armco advised the assessment team that attempts had been made to recycle the K061 material to the EAFs as briquetted material. These attempts did not develop into a feasible technique because the bulk of the hazardous constituents in the dust, i.e., cadmium, chromium, and lead, were either revolatilized or swept into the vent gases and reappeared in the EAF vent gas emissions. Another mitigating factor against reclamation of this material is the relatively low zinc level (10 to 12%). In EAF operations producing primarily carbon steels, the zinc level of the emissions is usually much higher, i.e., in the 15 to 20 percent range due to the high percentage of galvanized steel scrap used in the feed to the furnaces. In order for EAF dust to be economically attractive to reclaimers, it should have at least 15 to 20% zinc and preferably in the 25 to 50% range.

Because of the nature of the scrap Armco purchases for use in the EAFs and the products manufactured, i.e., stainless steels, it is highly unlikely that levels of chromium, cadmium, and lead could be reduced to the point where the EAF dust would pass the TCLP test, Toxicity Characteristic Leaching Procedure, which has now largely replaced the EP-toxicity testing procedure, which means that this waste must continue to be as RCRA listed waste K061. Thus, source reduction and recycling/reuse were ruled out as viable waste reduction options for reducing or eliminating the K061 waste generated at this plant. The only other approach available would be to detoxify this waste in a technically and economically feasible manner so that it could be disposed of in a nonhazardous landfill as a delisted waste. This approach, while not waste reduction, at least offered Armco the possibility of disposing of the waste as a nonhazardous material.

The current Best Demonstrated Available Technology (BDAT) regulations recently promulgated (August 8, 1988) by EPA specify that K061 waste be chemically stabilized before disposal in a hazardous waste landfill. This regulation is currently undergoing a U.S. Court of Appeals review based on appeals by the steel producers. EAF steel producers can, if their K061 waste is rich enough in zinc, ship this waste to zinc reclaimers using a high temperature roasting process, i.e., Horsehead Resource Development, Palmerton, Pennsylvania.

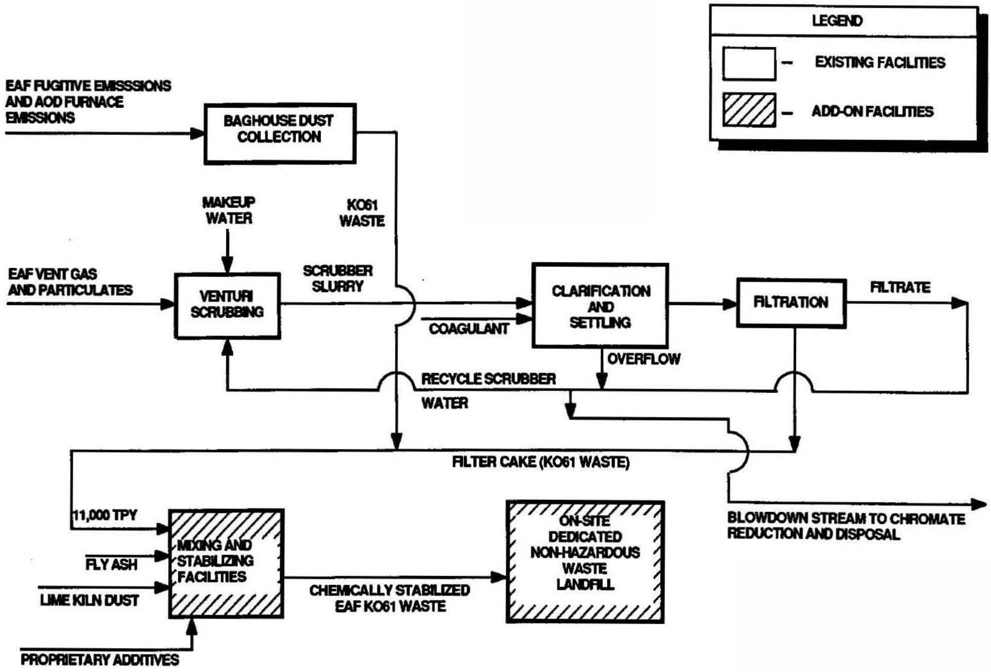

Figure 3. Simplified schematic of Versar-proposed modification of K061 waste treatment at Armco, Butler, PA., Main plant.

The assessment team proposed a detoxification option wherein the K061 waste is immobilized in an insoluble matrix using chemical stabilization of the combined venturi scrubber sludge filter cake/baghouse dust. Based on the pozzolanic reactions of materials containing anhydrous alumino-silicates (such as flyash), alone, or in combination with lime kiln dust and water, absorption and/or chemical stabilization of the heavy metals in the EAF dust would occur forming a calcium-alumino-silicate matrix, thereby rendering the quantities hazardous constituents in the dust essentially immobile. The use of small quantities of soluble silicates would tend to present leaching of chromium (the most leachable of the hazardous heavy metals present). Armco would need to perform laboratory-scale stabilization tests (including TCLP testing of the stabilized material) to establish optimum conditions needed to pass the EPA leaching criteria for delisting of this waste.

The assessment team felt that a stabilization procedure should yield a nonhazardous residue that could be land disposed on available land at the plant site. Besides resulting in a considerable saving in disposal cost, this proposal would eliminate the need to use outside hazardous waste landfills if the stabilization method proved to yield a delistable waste. The nonhazardous material would be produced in an add-on chemical stabilization system located in the melt shop area, and the chemically stabilized material would be disposed of in an on-site dedicated landfill. A simplified schematic of a detoxification process for the K061 waste is shown in Figure 3.

In a recent (September 1988) update of the Armco K061 waste handling situation at the Butler plant, it was learned that Armco is having the AOD baghouse dust (about 10% of the total K061 waste) briquetted offsite and subsequently blended into the EAF feed with satisfactory operating results to date. Currently, the EAF steel product mix at the Butler plant includes a significant percentage of carbon steels, such that the venturi scrubber sludge has a high enough percentage of zinc to permit acceptance of the sludge by a zinc reclaimer. Armco is presently able to recycle all of the K061 waste generated at the plant.

TABLE 2. CAPITAL AND OPERATING COST ANALYSIS FOR PROPOSED K061 WASTE STABILIZATION SCHEME AT THE ARMCO INC., BUTLER, PA PLANT

Capital equipment and facilities required for waste stabilization

Item	Cost, $
—Site preparation	$10,000
—Concrete mixing pad 20 × 25 × 1 ft thick; reinforced 35,000 psi RediMix concrete; side walls 30″ high; open ends	8,500
—Shelter bldg over pad area; 30 × 40 × 10 or 12 ft high; prefab steel corrugated roof and sides (could be reinforced fiberglass) Double doors both ends; unheated Complete, erected	25,000
—Electrical and water in shed	3,000
—Storage bin for lime dust (approx. 5 days supply); 12 × 12 × 25 Cone bottom; w/slide gate spout discharge and covered top with pneumatic fill attachment	18,000
—Bob-Cat front end loader; 3/4 CY bucket dedicated to K061 service; totally enclosed operators cab with fresh air intake particulate filter	60,000
—Front end Rototiller-type self-propelled mixer, 4 ft working width; enclosed operators cab with fresh air intake filter. Dedicated to K061 treatment	120,000
—1-6CY dump truck	45,000
—1-Bob-Cat front end loader for landfill operation	40,000
—1 Compacter, sheep-foot or equal	35,000
—1-Troxler Nuclear moisture gage, Model 3411	3,000
—2 Soil Test Penetrometers, Model CL-700 for compaction	100
Sub-total	367,600
20 percent contingency	73,500
Total capital	$441,100
Rounded	$442,000
Above estimates based on 1983–84 data; updated for 6 percent increase for labor, materials, and overhead, per annum	$526,000

Capital costs (on site stabilized waste disposal)

Landfill design based on EPA minimum technology guidance for single liner secure landfill (EPA/530-SW-85-013, May 24, 1985)

Item	Cost, $
Landfill installation cost, 11.25 acres × 100,000/acre[a]	1,125,000
Total capital costs (for stabilization facility and on-site secure landfill)	1,651,000
Cost of acquiring a RCRA Part B permit for an on-site TSDF[b]	100,000
Total capital cost	$1,751,000

Operating costs:

Item	Cost, $/Year
Lime kiln dust:[c] 11,000 TPY @ $10/ton delivered	110,000
Labor: $7.50/ton EAF waste[c]	83,000
Proprietary stabilizing materials (assumed)	10,000
Onsite disposal cost: 22,000 TPY @ $10/ton [3]:	220,000
Total operating cost	$423,000

Annual pre-tax operating savings of this option over present annual K061 disposal costs: $1,000,000-$423,000 = $577,000.

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[a] Based on actual costs obtained for new synthetic liner-equipped, leachate collection landfills; includes excavation, site preparation, membrane liner installation, and leachate collection and storage system.

[b] Armco estimate.

Feasibility Analysis Step

Based on the assessment team's evaluation of the available options, stabilization of K061 waste in an inpermeable matrix and disposal in an on site dedicated nonhazardous waste landfill, while not waste reduction, was believed to be the only technically viable option available to Armco. The assessment team proceeded to evaluate the economic viability of this option based on a study grade cost estimate. This economic evaluation follows.

The proposed alternative K061 waste treatment scheme involves treating a blend of 90% venturi scrubber sludge and 10% baghouse dust (approximately 11,000 TPY total, see Figure 2) with an equal weight of lime kiln dust and a small proportion of chemical additives (approximately 1% of the total mix) in an on-site blending operation. (Additives such as sodium silicate that would react with chromium to form an insoluble chromium silicate.) The EAF dust, sludge, and lime kiln dust are thoroughly mixed and then blended with additional water and appropriate special additives to approach within ±3% of the optimum water content (20–25%). This procedure was carried out to approach the desired physical and chemical properties in the final stabilized product.

The K061 waste stabilization scheme described has been subjected to a detailed capital and operating cost analysis. The information developed in this analysis is shown in Table 2.

Capital payback period available for this option (based on pre-tax annual savings) equals capital cost divided by net annual savings i.e., 1,751,000/1,000,000 = 3.0 years. Based on an economic life of 5 years (20% amortization per year), the internal rate of return is 20% [2]. The annual cost of stabilized waste preparation and disposal under this option is (\$423,000 + 350,000)/22,000 or \$35/ton, as compared to the current disposal cost of \$100/ton.

A preliminary report presenting the K061 waste stabilization option described (together with the economic analysis) was given to Armco's Butler plant environmental engineering personnel for their comments. Armco agreed with Versar's findings that this option (chemical immobilization of EAF dust and sludge, with subsequent delisting of the treated waters and disposal in a dedicated on site nonhazardous landfill) was the only feasible option (from both a technical and economic standpoint) available to them (source reduction and recycle/reuse options being ruled out). Armco also noted that, based on their own limited laboratory studies on EAF sludge immobilization, it may not be possible to satisfactorily immobilize hexavalent chromium using this technique. More extensive laboratory studies will be necessary to answer this point. In addition, it is noted that chemical stabilization of RCRA F006 electroplating sludge containing comparable or higher levels of chromium together with organics and other extraneous materials has been successfully demonstrated to meet TCLP criteria for total chromium [*4*].

The Versar assessment team recommended that the Armco, Butler main plant seriously consider the possibility of implementing the waste detoxification option for melt shop K061 waste. Waste generated by the EAF/AOD operations in the melt shop was being disposed of at the rate of 11,000 TPY in offsite TSDFs at cost of \$100 per ton. With source reduction and resource recovery options not available to reduce the quantity of this hazardous waste, the alternative proposed by the assessment team was to convert the material into a nonhazardous waste using a chemical stabilization technique, have the waste delisted by EPA, and dispose of this material in an on site dedicated landfill. A preliminary estimate of the cost of this option indicated a favorable payback period i.e., approximately 3 years with an internal rate of return of about 20%. Further, the disposal cost using this option was estimated as \$35/ton of treated waste compared to \$100/ton for the current cost of disposal of the raw waste. It was therefore recommended that this option be pursued further, with an initial bench-scale effort to establish the appropriate waste stabilization technique.

PLANT NO. 2 WASTE REDUCTION ASSESSMENT

Based on the information received by the assessment team, process and waste handling operations at Plant No. 2 were: the plant consists of a stainless steel strip annealing and pickling operation line for processing of series 300 and 400 stainless steels, and a waste acid neutralization plant. The facility anneals and pickles 300 and 400 series stainless steels. The plant pickling line pickles only Armco's stainless steel strip products and is composed of a Kolene treatment tank where the annealed steel sheet is treated with Kolene (a highly concentrated mixture of sodium hydroxide and potassium hydroxide) for descaling, a Kolene quench tank, two water rinse tanks in series, a nitric-hydrofluoric acid pickling tank, a final rinse tank, and a fume scrubber. A simplified schematic of the line is shown in Figure 4.

In the operation of the plant, stainless steel strip is received from the main plant located about 2 miles away. The stainless steel strip is first annealed and then descaled by the Kolene treatment, where oxide scale is removed by molten NaOH/KOH treatment at 800°F. The descaled strip is then rinsed to remove caustic materials and passed through a pickling operation where it is treated with a solution consisting of 2–4% hydrofluoric acid and 8–10% nitric acid. The pickled steel strip is then rinsed and coiled for shipment. The air emissions from the Kolene treatment and pickling acid tanks are all controlled by the use of wet scrubbers.

There were two corrosive waste streams (RCRA listed wastes K062) generated. The Kolene rinse water is highly alkaline and contains sodium and potassium hydroxides, sodium and potassium carbonates, and chromates resulting from some oxidation of the chromium on the steel surface during the Kolene descaling treatment. Chromate levels are below 200 ppm, and the spent rinse water has a pH of about 12. Spent pickle liquors and rinse waters from the pickling operations have a pH of about 2 and contain dissolved metals, nitrate, and fluoride. Approximately once per week, spent pickling acids (HF and HNO_3) are drained from the pickling tub, fresh acids are added, and a portion of the dumped spent acid is recycled. The spent pickle liquors contain 0–2% hydrofluoric acid and 0–8% nitric acid. They also contain dissolved nitrates and fluorides of cadmium, nickel, chromium, and iron. The excess spent pickle liquor is combined with the pickling line rinse water prior to being sent to the wastewater treatment facility. Average composition of the spent pickle liquor/rinse water stream over a one-week operation (which includes a once-per-week dump of the spent pickle liquor into the combined wastewater stream) is given as:

Parameter	Average Concentration, mg/l
Cr (trivalent)	164
Ni	47
Cd	<0.02
Fe	1,110
F	1,100
pH	~2.0

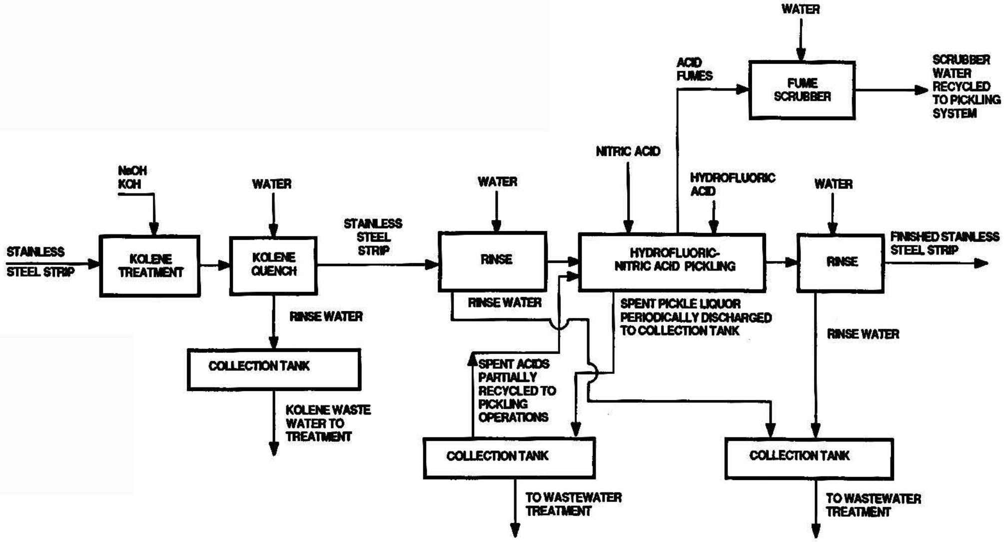

Figure 4. Simplified schematic of existing stainless steel surface treatment and pickling processes—Armco Plant No. 2, Butler, PA.

Volumes of wastes generated were about 5,000 gallons per week of the spent HF/HNO_3 pickle liquor are disposed of to the pickling line wastewater treatment system one batch basis. The combined wastewater stream from pickling operations including rinse waters and spent pickling acids, averages 150 gpm. Approximately 45 gpm of alkaline Kolene process rinse water was treated and disposed of.

Assessment Step

This phase of the waste reduction assessment began with a detailed inspection of the plant area by the Versar team. During this visit, the process flow was traced from the point of waste generation to the discharge of the treated K062 waste.

The hazardous waste management practice at Plant No. 2 involved pumping the combined spent acid and rinse water stream to the wastewater treatment plant where this stream is combined with treated Kolene waste and then neutralized. Raw Kolene rinse water is treated as follows: excess ferrous sulfate heptahydrate and sulfuric acid are added to the stream in a mix tank with about 80 minutes retention time. The ferrous ion reacts with chromate to reduce hexavalent chromium to trivalent chromium salts. The waste pH following treatment is approximately 4. The treatment of the combined waste stream was: the wastewater was pumped to a mix tank where slaked lime is added. The final pH after lime addition is about 8. The addition of lime causes the heavy metals present to precipitate as hydroxides and the fluoride to precipitate as calcium fluoride. The resulting mixture of treated wastewater and precipitated solids was treated in a second mix tank where coagulant is added and the stream is then fed to two 30-foot diameter clarifiers operated in parallel. The clear overflow from the clarifiers is discharged to the NPDES permit-controlled outfall (a local creek), and underflow is fed to two vacuum filters operated in parallel. Solids recovered from the filters (nonhazardous) were disposed of to an off site landfill and the filtrate was recycled to the treatment process.

The current treatment system yielded a treated wastewater containing about 21 ppm dissolved and suspended fluorides and negligible levels of heavy metals. The plant's present NPDES (Pennsylvania NPDES Permit #PA0006343) wastewater discharge permit requires that, effective at the end of 1988, the level of fluoride in the

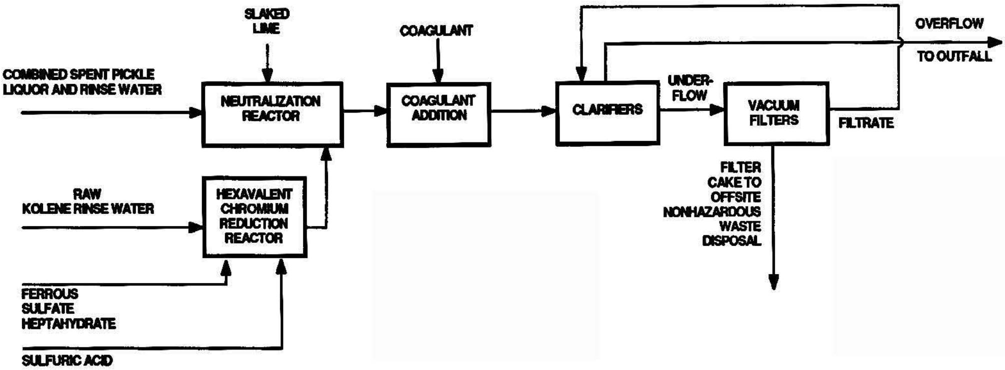

Figure 5. Simplified schematic of present wastewater treatment system, Armco Plant, Butler, PA.

final effluent (outfall 001) be reduced to 7 ppm. Figure 5 is a simplified schematic of the existing Plant No. 2 wastewater treatment system.

A review of possible waste reduction options at Plant No. 2 showed that Armco was already employing a source reduction technique by recycling a portion of the spent hydrofluoric acid/nitric acid pickling both to the pickling tank (see Figure 4). There did not appear to be any other major source reduction options available at the plant. In considering the possibility of recycle/reuse as a waste reduction option, the sludge resulting from treatment of the combined plant pickling line wastewater streams was studied. This sludge is a mixture of calcium sulfate, calcium fluoride, and small quantities of heavy metal hydroxides and there appeared to be no potential for reuse of this material. The raw waste, however, does contain a constituent that could be converted into a useful product—fluoride ion. Recovery of this ion as calcium fluoride (fluorspar) would require some modification of the existing treatment system.

The assessment team felt that an opportunity existed for recovering and utilizing calcium fluoride from the spent pickling acids and rinse water waste streams. The main plant melt shop presently purchases about 1,000 tons per year of fluorspar for use as a furnace flux material in the EAF steelmaking process with the current cost for this material being approximately $100 per ton at the plant. (Metallurgical grade material containing approximately 80% calcium fluoride is purchased in briquette form by Armco.) The assessment team proposed a waste reduction option for potential recovery of calcium fluoride wherein the combined plant wastewater stream at pH ~2 (excluding the treated Kolene waste) is treated with slaked lime at a controlled rate so that pH ~2.5 is not exceeded. Calcium fluoride would be selectively precipitated, and at this pH, fluoride solubility data in the literature indicate that a level of 65 ppm dissolved fluoride could be achieved. With about 1,100 ppm dissolved fluoride in the raw wastewater, approximately 95% of the fluoride is expected to precipitate. This is equivalent to about 1,300 tons per year of calcium fluoride potentially recoverable (based on 330 days per year operation), which more than equals the annual consumption of fluorspar flux in the EAF operation (930 TPY). Hydroxides of iron, nickel, and chromium are all highly soluble at pH values below 3.0 and thus would not co-precipitate with the calcium fluoride. Note that the recovered calcium fluoride was expected to assay better than 85% CaF_2, while the purchased metallurgical grade fluorspar averaged 77–80% CaF_2. This would actually enable the Melt Shop to reduce the amount of this flux added to each EAF heat by approximately 10%.

If the described option were to be put into operation by Armco, not only would the generation rate of sludge from K062 treatment be reduced (resulting in a saving in offsite sludge disposal costs), but a substantial potential savings in chemical purchases could be made. At the time of the assessment, Armco was disposing of approximately 4000 tons per year of nonhazardous sludge from Plant No. 2 wastewater treatment (in an offsite landfill) at a cost of $228,000 per year.

The necessary process modifications needed to recover solid calcium fluoride are shown in simplified schematic form in Figure 6 and consist of the combined A&P line #22 spent pickle liquor and rinse water discharge to be treated in the same waste acid neutralization system now used to generate the neutralized nonhazardous solids discharged off site and NPDES effluent to the outfall. However, the neutralization would be done in series in two stages, thereby effecting the recovery of a reasonably pure calcium fluoride in the first stage. After the first stage of neutralization, the presently treated Kolene waste would be combined with the partially neutralized waste pickle liquor/rinse water stream prior to final neutralization; the combined stream would then be neutralized and discharged to the outfall.

In the existing neutralization reactor (primary mix tank), slaked lime would be added to the combined pickle liquor/rinse water stream containing 1,100 ppm of fluoride, at a rate controlled to achieve a pH no higher than 2.5. At this pH, precipitation of fairly pure calcium fluoride would occur at the rate of 400 to 500 lb/hr. This slurry (with added coagulant) would then flow to one of the existing 30 foot diameter clarifiers where, after about

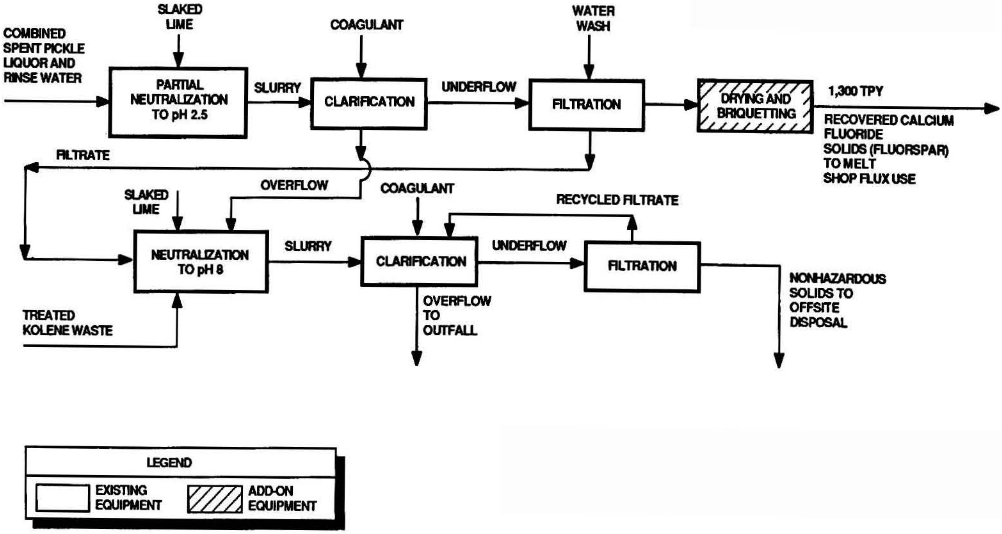

Figure 6. Proposed alternative treatment system for recovery of calcium fluoride from combined spent acid pickle liquor and rinse water at Armco Plant No. 2, Butler, PA.

one hour settling time, the underflow would flow to one of the two existing 6 ft × 6 ft vacuum belt filters. Following filtration, the filtered solids would be dried, briquetted and periodically transported to the melt shop area for use as flux in place of purchased fluorspar.

The combined clarifier overflow and filtrate from the vacuum belt filter and the separately treated Kolene waste would be pumped to the other existing 30 foot diameter clarifier where additional slaked lime and coagulant would be added to bring the final pH up to 8. At this pH, the residual fluoride and heavy metals would precipitate as calcium fluoride and hydroxides, respectively. It is expected that the achievable fluoride level would be near 7 ppm in the final effluent (the level required by December 31, 1988 by NPDES permit), because of the much lower amount of precipitated calcium fluoride available to be resolubilized in the second precipitation step. This would be an additional benefit achievable by this option. The settled slurry would then flow to the second existing 6 ft × 6 ft vacuum belt filter, where the solids are removed and discharged to a Vogel box. These solids would be nonhazardous and would be sent to off site disposal. The solids tonnage sent to offsite disposal would thus be reduced by approximately 30%, another economic benefit of this option. The clarifier overflow would be discharged to the local outfall.

It is believed that there is enough capacity available in the present clarifier/filter system in Plant No. 2 to allow the entire wastewater flow to proceed in series fashion through the two sets of clarifiers and filters. In the proposed first stage treatment step, calcium fluoride (with added coagulant) should settle much faster than the present calcium fluoride/metal hydroxide precipitate formed in the treatment plant. The latter material requires 8 to 10 hours residence time in the clarifier, while calcium fluoride (with added coagulant) should only need about one hour to adequately settle before the clarifier underflow is discharged to the vacuum belt filter.

Preliminary experimental verification and economic evaluation of this proposed calcium fluoride recovery option follow.

Feasibility Analysis Step

Versar performed bench-scale experiments to verify the technical feasibility of recovery of calcium fluoride from the spent pickling acid wastewater. A one-gallon sample

TABLE 3. CAPITAL AND OPERATING COST ANALYSIS FOR PROPOSED CALCIUM FLUORIDE RECOVERY SCHEME AT THE ARMCO INC., BUTLER, PA PLANT.

Capital costs	Installed Cost, $
Capital equipment requirements:	
• Drying (indirect gas-fired rotary dryer) and briquetting equipment to process 6.1 TPD of precipitated calcium fluoride (30% moisture) equivalent to 4.3 TPD of dry briquetted fluorspar equivalent.[a]	200,000
Existing equipment modifications:	
• Epoxy-coat one existing 30 ft diameter × 15 ft high carbon steel clarifier with 30 mil thickness of Bridgeport Chem. Corp. 6A70 (or equal) epoxy resin. Five-year warranty against liner failure	13,000
Complete (labor and material)[b]	
Epoxy-coat lime neutralization reactor tank[a]	2,000
• Rubber-line all exposed carbon steel parts of one existing 6 ft × 6 ft Ametek rotary vacuum filter (job done at vendor shop)[c]	50,000
• Rubber-line all piping and pumps exposed to pH 2.5 environment. Replace all valves and fittings with appropriate acid-resistant material[b]	30,000
Instrumentation changes required:	
• pH control on first neutralization stage required to be more sensitive and reliable than currently available at Plant No. 2	5,000
Estimate for pH equipment replacement[d]	
TOTAL INVESTMENT COST	$300,000
Operating cost (330 days/year 8 hours/day for drying and briquetting operations)	Cost, $/yr
Precipitation/neutralization system:	—
No significant increase in precipitation/neutralization system operating cost expected over present operating cost of wastewater neutralization system. Lime consumption should actually decrease because of closer pH control in neutralization operation	
• Drying of 6.1 TPD precipitated calcium fluoride (dry 70% solids stream to <1% moisture in indirect gas heated rotary dryer using natural gas firing). With cost cost @ 4.00/MM BTU and energy utilization efficiency of 50%, drying cost is $2.40/1000 lb feed	1,000
• Briquetting of dried calcium fluoride @ $1.00/1000 lb feed to one-inch, roughly spherical briquettes (no binder required)	3,000
• Direct labor and supervision (0.6 persons @ $20/hr)	29,000
• Maintenance costs (labor and materials) for drying and briquetting equipment @ $0.50/1000 lb feed	4,000
TOTAL ANNUAL OPERATING COST	$46,000
Savings due to replacing purchased fluorspar, 1000 TPY @ $100/ton	$100,000
Savings due to lower cost of offsite landfill disposal ($228,000/yr × .30)	68,000
GROSS ANNUAL SAVINGS (Pretax)	$168,000/year
Net annual savings =$168,000-$46,000 = $122,000/year	
Payback period required: 300,000/$122,000	2.5 years

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[a] Vendor equipment estimates and assessment team installation cost estimates.
[b] Estimate provided by Tank Coatings, Inc., Pittsburgh, PA.
[c] Estimate by Rubber-Covered Products, Smithfield, RI.
[d] Assessment team estimate.

of spent hydrofluoric/nitric acid pickle liquor (not diluted with rinse water) was obtained from the Armco Plant No. 2 pickling line facility during the detailed plant inspection visit. An initial small-scale experiment was performed on this sample.

One 20 ml sample of the spent HF/NHO_3 pickle liquor was treated with 1.07 grams of anhydrous calcium chloride. The calcium chloride was dissolved by stirring into the pickle liquor. The pH of the resulting solution was then recorded as 1.67. The solution was then adjusted to pH 2.1 with saturated lime water. About 100 ml of lime water was added to raise the pH to the desired value. A white precipitate (possessing a greenish tinge) of calcium fluoride slowly formed and settled from the solution over about a one-hour period. The slow settling of the finely divided calcium fluoride indicates the need to add a coagulant (such as alum) in relatively small quantities, i.e., <100 ppm, to achieve rapid agglomeration and settling of the precipitated material. The solution was then filtered and samples of the filter cake and filtrate were forwarded for analysis. The filtrate was then treated with additional lime and lime water until pH 8 was reached. The solution was then again filtered, and samples of the filtrate and filter cake were forwarded for analysis.

Analyses for fluoride, nitrate iron, total chromium, hexavalent chromium, and nickel were then run on the two filter cake and two filtrate samples resulting from the above experiment. Results indicate that a relatively pure calcium fluoride material can be selectively precipitated at pH 2.5. Analysis of the material produced at this pH indicated about 80–85% calcium fluoride, approximately 13% iron fluoride, and about 1% chromium as chromium fluoride. This material should be directly usable as fluorspar flux (following drying and briquetting) in the EAFs at the melt shop and this recycle option appeared to be technically feasible.

In this recycle option, the assessment team proposed use of the existing lime neutralization reaction tanks, clarifiers, and filters available in the present wastewater treatment system. In order to handle the pH 2.5 wastewater, which is quite corrosive to carbon steel, it was proposed to epoxy-coat the existing lime mix tank, the clarifier, and to rubber-cover all exposed parts of one rotary vacuum filter, as well as all interrelated piping and pumps. All valves and fittings exposed to the pH 2.5 environment would be replaced with suitable acid-resistant materials. The other existing clarifier and rotary vacuum filter system exposed only to a pH 8 environment would continue to operate as carbon steel units. Since one clarifier/vacuum filter system can handle the present wastewater flow, if one of the other sets of these units were to go down for repairs, there would always be redundancy available in this system, i.e. the clarifier/filter system operating in the pH 2.5 mode could immediately switch to pH 8 operation (full neutralization without calcium fluoride recovery), in the event either of the other clarifier or filter units went down. As a further backup in the event of unavailability of this system for recovery of fluorspar, a suitable quantity of commercial fluorspar would always be kept on hand in the melt shop. It is envisioned that the revamp of the process units and related equipment would be accomplished during a plant turnaround, i.e., over a two-week period.

The calcium fluoride scheme described above has been subjected to a detailed capital and operating cost analysis. The information developed in this analysis is shown in Table 3. The payback period shown is shorter than is the usually acceptable yard stick for favorable investment payback (3 years). Based on an economic life of 5 years (20 percent amortization per year), the internal rate of return is approximately 28 percent [2].

A preliminary report presenting the fluorspar recovery option for Plant No. 2 HF/HNO_3 pickling waste were presented to Armco's Butler engineering personnel at a meeting on August 29, 1986. Armco expressed considerable interest in this proposed option: selective recovery of calcium fluoride at a controlled pH of 2.5 with subsequent use of this material (fluorspar) as a metallurgical flux in the main plant melt shop. The implementation of this option was to be seriously evaluated by Butler management.

SUMMARY

The Versar assessment team determined that Plant No. 2 generates a spent HF/HNO_3 pickling acid/rinse water waste stream (K062) that is currently neutralized with lime, the waste solids disposed of in an offsite nonhazardous waste landfill (approximately 4000 TPY) at an annual cost of $228,000, and the treated wastewater disposed of to a local stream under a NPDES permit. Following is a resource recovery option that was recommended for this waste.

Recovery of the bulk of the fluoride ion present in the raw HF/HNO_3 spent acid/rinse water waste stream as calcium fluoride by selective precipitation using lime and controlling pH so that the latter not exceed pH 2.5 (approximately 95 percent of the calcium fluoride can be recovered by this method). After clarification and filtration, the recovered calcium fluoride (approximately 1300 TPY valued at $130,000 based on Armco's present purchase price for this material) is dried, briquetted and used as metallurgical flux in the melt shop operation, replacing presently purchased material. Following calcium fluoride recovery, the partially neutralized spent acid/rinse water stream is fully neutralized as is done in the present waste water treatment operation at Plant No. 2. In addition to recovering a valuable product (fluorspar) for in-plant use, implementation of the option would reduce Armco's solid waste disposal cost at Plant No. 2 by approximately 30 percent. Versar also believes that an additional benefit would be the ability of the final neutralization step (following the selective fluoride precipitation step) to achieve the fluoride discharge level at the NPDES outfall i.e., 7 ppm fluoride, by 1988.

The team recommended that Armco give serious consideration to retrofitting one existing clarifier and one rotary vacuum filter to convert these units for corrosion resistant operation in order to operate in a pH 2.5 environment. These units would always be available to operate in the present pH 8 full neutralization mode if either the other clarifier or vacuum filter are disabled and down for repairs.

ACKNOWLEDGMENT

The authors gratefully acknowledge the generous support provided by Mr. Harry Freeman, Waste Minimization Branch Chief, Risk Reduction Engineering Laboratory, U.S. EPA Office of Research and Development, Cincinnati, Ohio.

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Biodenitrification of Uranium Refinery Wastewaters

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Design verification studies and process development work were conducted at Oak Ridge National Laboratory in support of the new fluidized-bed biodenitrification system under construction at the Feed Materials Production Center (FMPC) in Fernald, Ohio. Two bioreactors in series, each 6-m tall, and one 12-m-tall bioreactor were operated for approximately 9 months using synthetic and actual wastewaters from the FMPC. The results indicate that satisfactory reaction rates can be achieved and maintained; however, some degree of water softening, pH adjustment within the bioreactors, and temperature control may be necessary.

INTRODUCTION

The Feed Materials Production Center (FMPC) in Fernald, Ohio, generates as much as 800 L/min of a composite aqueous waste stream containing up to 10 g/L of nitrate. The principal source of the nitrates is the raffinate from a solvent extraction process used in the production of uranium metal for the U.S. Department of Energy (DOE).

In order to treat this waste stream to meet nitrate discharge limits, a fixed-film, fluidized-bed biodenitrification facility was designed on the basis of pilot development work done at Oak Ridge National Laboratory (ORNL) in the late 1970s [*1, 2*]. The biodenitrification plant design consists of four 12 m tall, 1.3 m diameter fluidized-bed bioreactors of the ORNL design, including a vibrating screen filter for the effluent from each column. The four columns are to be operated in series to achieve the necessary liquid holdup time to produce an effluent containing less than 0.1 g/L of nitrate. The existing and proposed wastewater treatment systems at the FMPC are shown in Figure 1.

Since the design of the FMPC biodenitrification plant involves significant extrapolation of the ORNL system to larger equipment and actual rather than synthetic wastewaters, ORNL was asked by DOE to review the FMPC design and to perform an experimental design verification study. This paper reports the results of this study.

BIOLOGICAL DENITRIFICATION

Bacteria are able to remove nitrate from wastewaters by converting the nitrate to gaseous nitrogen. This is accomplished under anoxic conditions, with the NO_3^- serving as the terminal electron acceptor for microbial respiration in the absence of molecular oxygen. A carbon source such as methanol, ethanol, or acetate must also be present to act as an electron donor. The bacteria responsible for denitrification are facultative and utilize the same biochemical pathways during both aerobic and anaerobic respiration. However, different enzymes catalyze the terminal electron transfer [3].

The general equation for biological denitrification is

$$NO_3^- + \text{carbon source} \xrightarrow{\text{microorganisms}} N_2 + CO_2 + H_2O + OH^- + \text{cells} \quad (1)$$

This production of hydroxide ions may cause the pH within the bioreactor to rise. Several studies have shown the denitrification rate to be a function of the pH. These studies have generally shown the optimum pH for biological denitrification to be in the 6.5 to 8.0 range; outside this range the rate of denitrification decreases sharply [3–7]. Also, since denitrification is an exothermic reaction, a temperature rise within the bioreactor may occur.

ORNL BIODENITRIFICATION REACTORS

In the fluidized-bed bioreactor process developed at ORNL, bacteria are allowed to grow and attach to 30- to 60-mesh anthracite coal particles to form "bioparticles." The wastewater is pumped up through a bed of bioparticles at a velocity sufficient to fluidize the bed. As the wastewater flows past the bioparticles, the nitrate is degraded and N_2 and CO_2 gas are produced and vented to the atmosphere.

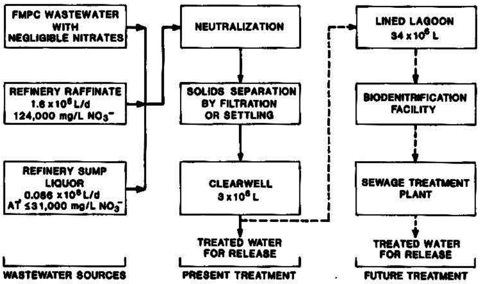

Figure 1. Old and new wastewater treatment schemes at the Feed Materials Production Center, Fernald, Ohio.

The 12 m high bioreactors at the FMPC were simulated at ORNL using two different bioreactor systems. One bioreactor system contained two 10 cm diameter, 6 m high glass bioreactors operated in series. The other system was a single 10 cm diameter, 12 m high bioreactor constructed from PVC pipe. The shorter reactors in series were used to simulate the FMPC bioreactors because previous work at ORNL had shown the denitrification rate to be independent of the reactor diameter and dependent on the hydraulic residence time within the bioreactor over a wide range of diameters from 2.5 cm to 50 cm [2]. Both systems had sample ports located every 1 to 1.3 m along the length of the bioreactors so that parameters of interest could be followed as a function of position within the bioreactors.

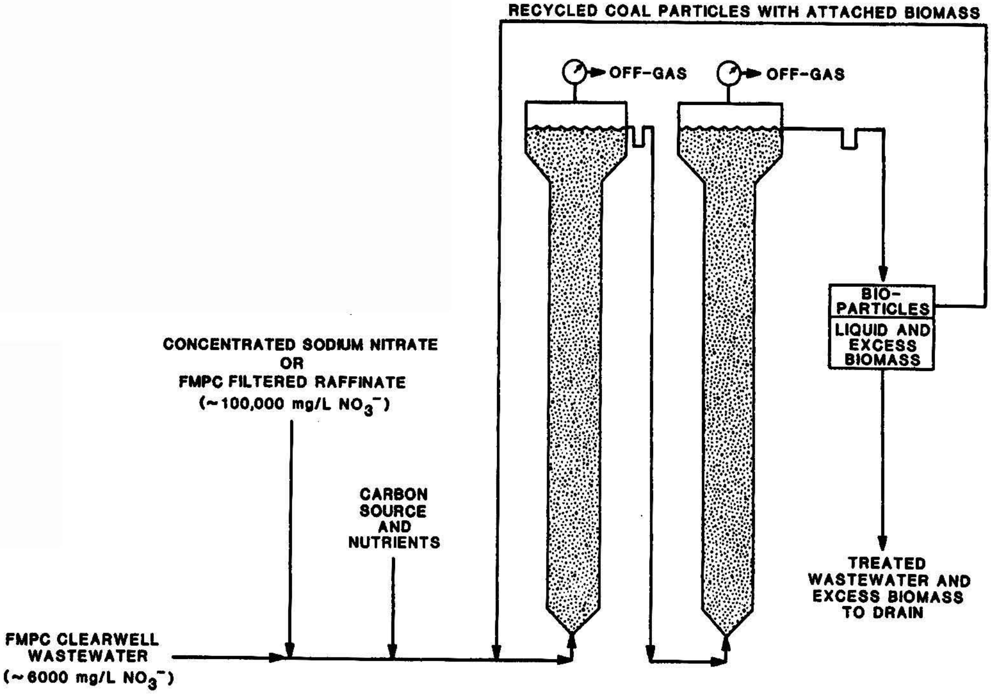

Figure 2. Schematic representation of the series bioreactors system at Oak Ridge National Laboratory.

A schematic diagram of the two-bioreactors-in-series system is presented in Figure 2. The wastewater from the FMPC clearwell (~600 mg NO_3^-/L) was mixed with either softened raffinate or a concentrated sodium nitrate solution to give a nominal inlet nitrate concentration ranging from ~7000 to 10,000 mg NO_3^-/L. A carbon source (methanol or ethanol at ~1 g carbon/g nitrogen) and nutrients were added to the wastewater before it was pumped into the bottom of the bioreactor. The volume and flow of N_2 and CO_2 gases produced in the first reactor were continuously monitored and recorded by a wet-test meter equipped with an electronic pickup before being vented to the atmosphere. The wastewater and entrained bioparticles overflowed the first bioreactor and were pumped into the second bioreactor. The process was repeated in the second bioreactor, with the liquid and entrained bioparticles passing to a vibrating-screen filter that served as a liquid/solid separator. The filter was designed to remove the excess biomass from the bioparticles and to recycle the bioparticles to the inlet of the first bioreactor. The excess biomass and broken coal particles were discharged from the system with the effluent from the second bioreactor.

In the second pilot facility, minor modifications were made to improve the operability of the biosystem; however, the process was essentially identical to the first, except for the change to a single tall bioreactor to more closely simulate an FMPC bioreactor.

DESIGN VERIFICATION STUDIES

Each of the four FMPC bioreactors is designed to operate at an average denitrification rate of ~30 kg N/d · m^3. This rate was based on previous pilot work at ORNL. However, review and comparison of the FMPC design and the previous ORNL studies revealed several differences that raised concerns about the operability of the FMPC bioreactors. As a result of these concerns, various combinations of synthetic wastewater and actual wastewater shipped to ORNL from the FMPC were used to perform design verification studies of the FMPC bioreactors [7]. The concerns raised during the design review and the major findings from the design verification studies are discussed below.

Calcium Carbonate Precipitation

The FMPC uses lime to neutralize the wastewater from the solvent extraction raffinate; therefore, the raw wastewater being fed to the FMPC bioreactors will have high concentrations of calcium. Because carbon dioxide is produced during the denitrification reaction, it was anticipated that calcium carbonate would precipitate and possibly interfere with the reduction of nitrates. To determine if this would occur, a study was conducted using a combination of ORNL process water and FMPC wastewater, with the percentage of FMPC wastewater being increased with time. The two-column pilot biosystem was operated for three distinct periods; ~one week on a mixture of 17% FMPC wastewater and 83% tap water; ~two weeks on 34% FMPC wastewater; and ~1.5 weeks on 100% FMPC wastewater.

While operating on 17% FMPC wastewater, the feed to the pilot biosystem contained ~1 g of nitrate per liter and from 75 to 100 mg of calcium per liter. During this time the denitrification rate reached 6 to 8 kg N/d · m^3. It also became evident that calcium carbonate was precipitating and accumulating on the bioparticles within the bioreactor.

During the following two weeks, while operating at 34% FMPC wastewater, the feed to the pilot biosystem contained ~2 g of nitrate per liter and from 150 to 200 mg of calcium per liter. During this period the denitrification rate increased slightly to 8 to 10 kg N/d · m^3. However, the buildup of calcium carbonate began to plug lines and accumulated on the bioparticles to such an extent that the bed was difficult to fluidize.

When the biosystem was switched to 100% FMPC wastewater, which contained ~6 g of nitrate per liter and ~450 mg calcium per liter, biodenitrification ceased within one week. This was attributed to the accumulation of calcium carbonate on the bioparticles, which interfered with the maintenance of active biomass within the bed.

These observations of calcium carbonate precipitation in the bioreactor are consistent with the CO_2/carbonate equilibria, the solubility of calcium carbonate, and the quantitative generation of CO_2 from the biodenitrification reaction. For a particular biodenitrification rate, the amount of CO_2 added to the liquid phase can be estimated from the reaction stoichiometry. The distribution of this CO_2 among carbonate, bicarbonate, precipitated calcium carbonate and dissolved CO_2 can be estimated using the measured pH, classical ionic equilibria and solubility product, and material balances on calcium, and total CO_2.

A series of curves is shown in Figure 3. For example, when the biodenitrification rate is 10 to 15 kg N/d · m^3 and the pH is greater than 8, the effluent liquid will contain about 50 mg/L of calcium in solution. The balance of the calcium will be precipitated as calcium carbonate; certainly some of this precipitate will be deposited on the bioparticles. These conditions are representative of the operation of the biosystem described above.

The calculations represented in Figure 3 indicate that more than 50 mg/L of calcium can be maintained in solution if the pH is controlled at or below 7 for biodenitrification rates in the range of 20 to 30 kg N/d · m^3, which is the target range of performance. Subsequent experimen-

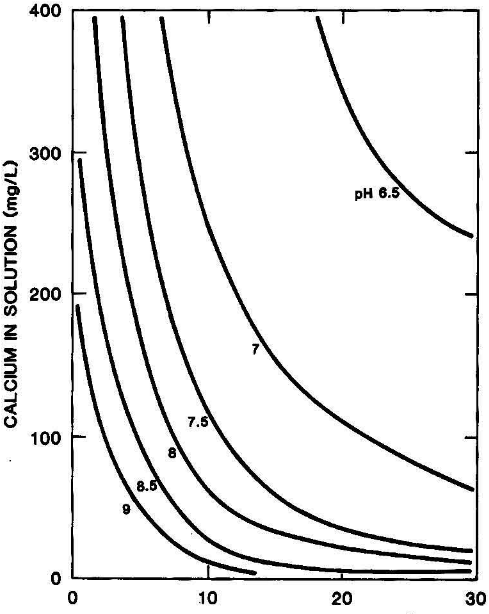

Figure 3. Solubility limit for calcium following production of carbon dioxide by the biodenitrification reaction (see text).

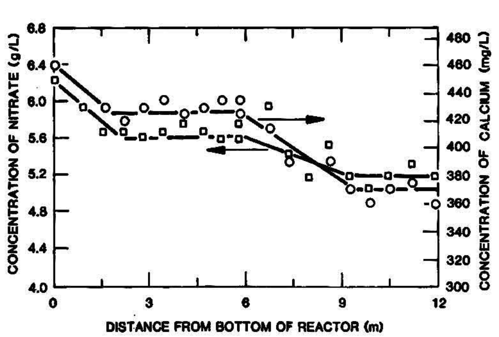

Figure 4. Typical axial profiles of nitrate and calcium concentrations in the series bioreactors system. □ = nitrate; ○ = calcium.

tal studies with the 12 m bioreactor indicated that a calcium concentration of 50–100 mg/L can be treated successfully without undue buildup of carbonate.

It is interesting to compare the concentration profiles for calcium and nitrate along the height of the bioreactor before the buildup of calcium carbonate caused the shutdown of the biosystem. As seen in Figure 4, both nitrate and calcium are being removed in approximately the first 2 m of the first bioreactor and in approximately the first 3 m of the second bioreactor. This suggests that the carbon dioxide produced by the microorganisms was immediately being converted to calcium carbonate. The rate of denitrification, rather than the calcium concentration, was probably controlling the deposition of calcium carbonate.

Bioreactor Height and pH

Previous studies at ORNL had shown that, as the nitrates are broken down, the pH rises to ~9 at the effluent from a 6 m high bioreactor. It has been further shown and corroborated by several studies that, as the pH rises above the 6.5 to 8.0 range, the denitrification rate decreases substantially [3–6]. Both synthetic and softened FMPC wastewaters were used in the pilot systems to determine if the pH would rise enough in a 12 m high bioreactor to inhibit biodenitrification. Figure 5 is a typical pH profile while operating on synthetic wastewater. As can be seen, the pH climbs to ~9 in the first bioreactor (representing the first 6 m of the FMPC bioreactor) and remains at ~9 for the entire 6 m of the second bioreactor. For comparison, the nitrate profile obtained from analysis of the same samples is also presented in Figure 5. As the pH climbed above ~8, the nitrate degradation fell sharply. By the time the pH had climbed to ~9, no nitrate was being degraded.

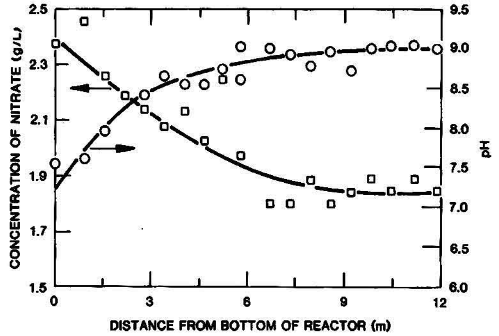

Figure 5. Typical axial profiles of nitrate concentration and pH in the series bioreactors system. □ = nitrate; ○ = pH.

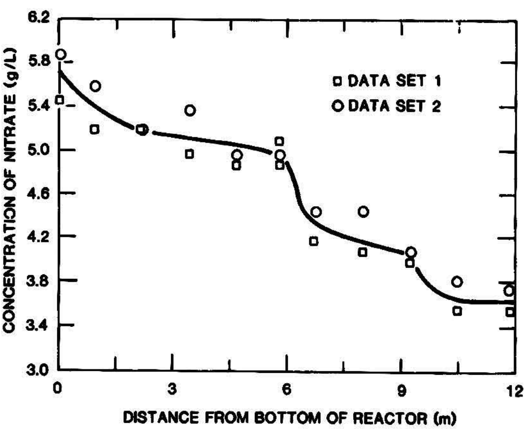

Figure 6. Typical axial profile of nitrate concentration in the series bioreactors system with pH adjustment (acid addition) between the two bioreactors (6 m) and halfway up the second bioreactor (9 m). Two different data sets are shown.

A pH control system was added to the inlet of the second bioreactor (representing the second 6 m of the FMPC bioreactor) to return the pH of the wastewater back to ~7. Additionally, acid was metered into the system at the 3 m point in the second bioreactor. A plot of a typical nitrate profile under these conditions is presented in Figure 6. As can be seen, at each acid addition point (0, 6, and 9 m levels) there is a sharp increase in the denitrification rate. After the implementation of acid additions, the denitrification rate for the total biosystem more than doubled and reached 30 to 40 kg N/d · m^3.

Raw FMPC wastewater was softened using sodium carbonate to reduce the calcium concentration to <5 mg/L. The softened FMPC wastewater appeared to have a buffering capacity such that the pH rise within the bioreactor was less than with the synthetic wastewater. This buffering capacity is evident in Figure 7, which shows the reactor pH profiles on the day the softened FMPC wastewater was first added to the pilot biosystem and the day prior to the addition. The less dramatic rise in the second bioreactor can be attributed to acid addition halfway up

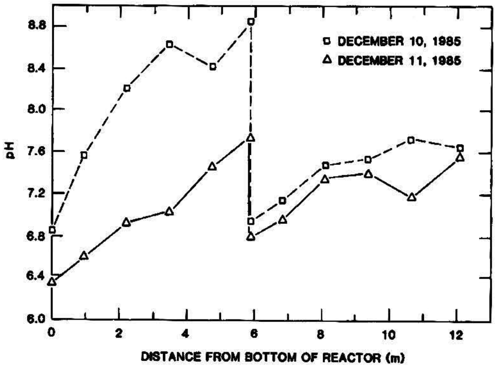

Figure 7. Comparison of the axial pH profiles in the series bioreactors system immediately before (□) and the day after (△) the change from synthetic wastewater to softened FMPC wastewater. The discontinuity at 6 m is because of pH adjustment between the two 6 m columns.

TABLE 1. COMPARISON OF THE THEORETICAL AND MEASURED TEMPERATURE RISE IN THE 12 m PILOT BIOREACTOR AT VARIOUS DENITRIFICATION RATES

Denitrification Rate, kg N/d · m³	Theoretical Temperature Rise, °C	Experimental Temperature Rise ± Standard Deviation, °C
8	1.5	0.93 ± 0.50
20	3.7	3.59 ± 0.52
30	5.5	4.46 ± 1.11

the second bioreactor (9 m level). This buffering capacity was accompanied by a corresponding increase in denitrification rate.

The addition of acid within the bioreactor at selected locations appears to be an effective means of mitigating the pH rise and thus, maintaining high reaction rates. Sulfuric, acetic, and phosphoric acids were used in these studies with equal performance. The amount of acid required, or perhaps the need for acid at all, depends on the natural buffering capacity of the wastewater.

Temperature Rise Within the Bioreactor

Resistance temperature devices (RTDs) were installed along the length of the 12 m pilot bioreactor to measure the temperature at various locations within the bioreactor. Experimental results and theoretical predictions are shown in Table 1 for several periods in which the experimental biodenitrification rates were stable over several days. The free energy of reaction has been reported to be −138.6 kcal per mol of methanol [6], which is the basis for the theoretical calculations. For the total bioreactor height of 48 m at the FMPC, the total temperature rise (under adiabatic conditions) would be about 20°C at the design reaction rate. Temperature control of some sort may be needed to maintain an acceptable temperature for the biological activity. However, the temperature dependence of the biodenitrification rate is not well characterized.

Stable Bioreactor Operation

In order to maintain high denitrification rates (≥30 kg N/d · m³), relatively constant feed conditions and thin, active biofilms within the bioreactor must be maintained. In these studies, as in previous ORNL studies, it was found that changes in the feed composition frequently caused a significant drop in the denitrification rate. This drop was usually short-lived, and the denitrification rate returned to its previous level within 48 hours after the microorganisms had adapted to the new feed conditions.

Daily addition of from 2% to 5% of the reactor bed volume with fresh coal particles helped to maintain thin, active biofilms. This addition forced the larger, less active bioparticles out of the top of the bioreactor and into the vibrating-screen filter. The vibrating screen scrapes off the less active biomass and recycles the bioparticle back to the inlet of the bioreactor.

The off-gas production rates from the ORNL biodenitrification systems were continuously monitored during the design verification study. These off-gas rates were then compared with the denitrification rates based on the analyses of the wastewater from inlet and effluent samples (Figure 8). The off-gas rates agreed well with the values predicted by denitrification stoichiometry using both ethanol and methanol as a carbon course. As a result, the off-gas production rate proved to be a reliable indicator of real time performance of the biosystem.

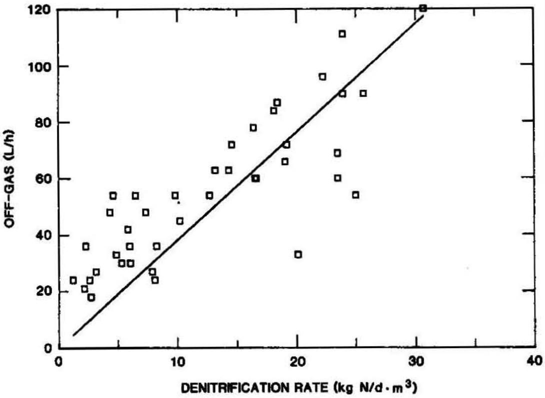

Figure 8. Comparison of the off-gas rates and the denitrification rates as calculated from the inlet and effluent nitrate concentrations over 3 months of operation of the single 12 m bioreactor. The line is a least-squares fit, forced through the origin, and has a slope of 3.8 L/h of off-gas per kg N/d · m³. The theoretical slope is approximately 4.

CONCLUSIONS

Fluidized-bed biodenitrification is expected to be effective technology for treatment of the nitrate-containing wastewaters at the FMPC. The only significant accommodation for biotreatment of the wastewater appears to be the restriction of the calcium concentration to ~50 mg/L. To accomplish this, the FMPC has installed a softener for the feed water to the bioreactors. Two of the four full-scale biodenitrification reactors are now successfully treating a reduced flow of wastewater without the need for acid addition within the reactors or temperature control. The remaining two bioreactors are not needed at present.

ACKNOWLEDGMENTS

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Effective Reduction of Emissions From Resource Recovery Operations

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The emission control system for the Commerce California Resource Recovery Facility is a Teller semi-dry unit using lime as neutralizing agent and a phonolite (Tesisorb) dry venturi injection material. The system, installed in 1987, has exhibited a 98% on-line reliability. The system emissions for particulate and acid gases were approximately one-third of the California regulations. The uniqueness in performance was the reduction of the respirable particulates to less than 0.5 mg/Nm^3 and the reduction of dioxins, toxic equivalent to less than 0.009 ng/Nm^3.

INTRODUCTION

Concomitant with the increasing use of resource recovery systems is the emergence of knowledge of the emissions from the combustion process. It is increasingly evident that they represent potential hazards. We have currently identified the following in the gaseous emissions:

- visible particulates
- fine respiratory ingestible particulates that act as carriers for heavy metals and dioxins
- toxic heavy metals (non-volatile)
- mercury
- hydrochloric acid
- sulfur dioxide
- sulfur trioxide
- hydrofluoric acid
- nitrogen oxides
- volatile organic compounds including chlorinate organics
- dioxins and furans

Whether these materials and compounds are emitted in concentrations and quantities that can result in pathological effects on humans, injury to agricultural crops, cattle, and structures, is not known.

Because resource recovery is both a technological and social problem, the task is to satisfy communities with reduction of emissions to the lowest achievable levels.

COMMERCE RESOURCE FACILITY

In 1984 the Los Angeles Sanitation District, the developer of the City of Commerce Resource Recovery facility, decided to provide an emission control system to comply with existing regulations and to achieve the lowest achievable emissions (Table 1). The Teller system, which had already demonstrated reliable performance in producing emissions lower than the regulatory limits for particulates and acid gases in the United States and Japan, was selected (Figure 1).

This emission control system [1, 2] consists of three major components:

1. An upflow quench reactor to enhance drying effectiveness, essentially doubling the drying time for the same geometric configuration and flow as a downflow reactor (Table 2).

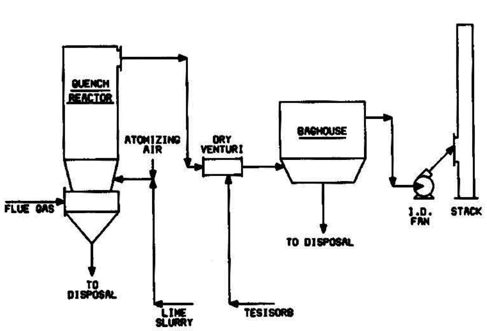

Figure 1. Air quality control system.

TABLE 1. COMPARISON OF PERFORMANCE AND REQUIREMENTS—TELLER SYSTEMS, CITY OF COMMERCE.

	Permit Limit	Guarantee Limit	Design Objective	Performance
Total Particulate				
GR/DSCF (corr. 12% CO_2)	0.016	0.007	0.004	0.0043
mg/Nm^3 (corr. 12% CO_2)	36.6	16.0	9.3	9.8
Fine Particulate (<2m)				
GR/DSCF (corr. 12% CO_2)	NA	NA	0.002	0.0002
mg/Nm^3 (corr. 12% CO_2)	NA	NA	4.7	0.47
HCL PPMDV (corr. 3% O_2)	NA	70	3 5	11.3
Percent Reduction	NA	90	95	98.5
SO_2 PPMDV (corr. 3% O_2)	26.8	47	21	1.56
Percent Reduction	80	80	90	99 5
HF PPMDV (corr. 3% O_2)	NA	NA	0.5	0.049
Percent Reduction	NA	NA	95	99.8
Heavy Metals (1)				
mg/Nm^3 (corr. 12% CO_2)	NA	NA	0.7	<0.18
Percent Reduction	NA	NA	NA	99.8
Hydrocarbons PPMDV as C_1				
by CARB 1-100	<1	NA	<1	<1
by TCA/FID	37	NA	37	<21
Chlorinated Hydrocarbons				
PPB	NA	NA	10	<6 (incl. ND limit)
— Total PCDD ng/Nm^3	NA	NA	≤2.2	<0.61
— Toxic Equiv. PCDD ng/Nm^3	NA	NA	≤0.2	<0.009

NA — Not Applicable
(1) — Exclusive of Mercury

2. Dry venturi to modify the particulate characteristics to permit a longer residence time for the collected particulate and reagent in the baghouse with no increase in pressure drop.
3. Baghouse that serves as a final fixed bed neutralization reactor and absorbent bed because of the accumulation of a thick cake, with efficiencies of 95% for acid gas and dioxin recovery.

Although the system had performed well for the recovery of acid gases, particulates, and heavy metals, there had been no effective confirmation of its behavior for the control of volatile organic compounds and the dioxin-furan group.

The prevailing view at the time of design was that dioxins, formed in the furnace, could be destroyed by operating the combustion process in the range of 900–1,000°C, with a residence time of 1 to 2 seconds. However, there was increasing evidence that dioxins were also formed downstream of the furnace, generally in the boiler zone in the temperature range from 200°C to 500°C [*3, 4, 5, 8*]. As a result, provision was made for capture of dioxins within the emission control system by establishing conditions described in the proprietary process [6] for activated adsorption of dioxins and furans on flyash and silica-alumina Tesisorbs (generally phonolite or nepheline syenite for incineration systems).

This process requires reduction of the gas temperature in the baghouse to the range of 120°C and filtering the gas through a fixed bed containing flyash and silica-alumina components, the enhanced thickness baghouse cake, inherent in the Teller system.

The increased thickness of cake in the baghouse had demonstrated modulation of the high variation (±50%) in acid gas concentrations emitted by the incinerator, without the imposition of sophisticated controls. Because the variation in concentration occurs in intervals as low as 2 minutes (Figure 2), effective response of instrumentation to vary the reagent feed is extremely difficult.

However, because of the thick cake created by the dry venturi action, excess reagent and adsorbent are stored on the bags and provide an effective fixed-bed adsorber-reactor. Efficiencies of acid recovery and adsorption of

TABLE 2. EFFECTIVE DRYING TIME—UPFLOW AND DOWNFLOW QUENCH REACTORS BASED ON MODEL ANALYSIS.

Inlet Temp.	400°F
Water Content	12%
Outlet Temp.	285°F
Quenched Gas Vel.	5 fps

Spray Size Distribution Micron Size				Length of Quench Reactor Required Ft.	
100	140	250	350	Upflow	Downflow
0	0	0	100	22.5	49.6
0	95	0	5	24.8	58.5
80	10	6	4	24.5	57.4

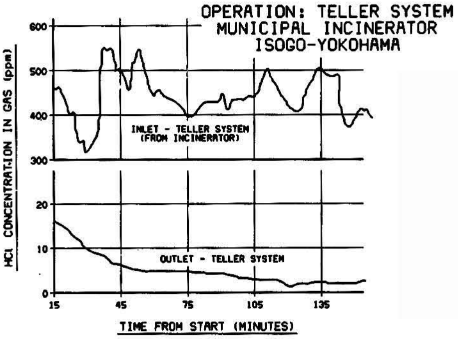

Figure 2. Effect of fixed bed reagent accumulation in baghouse.

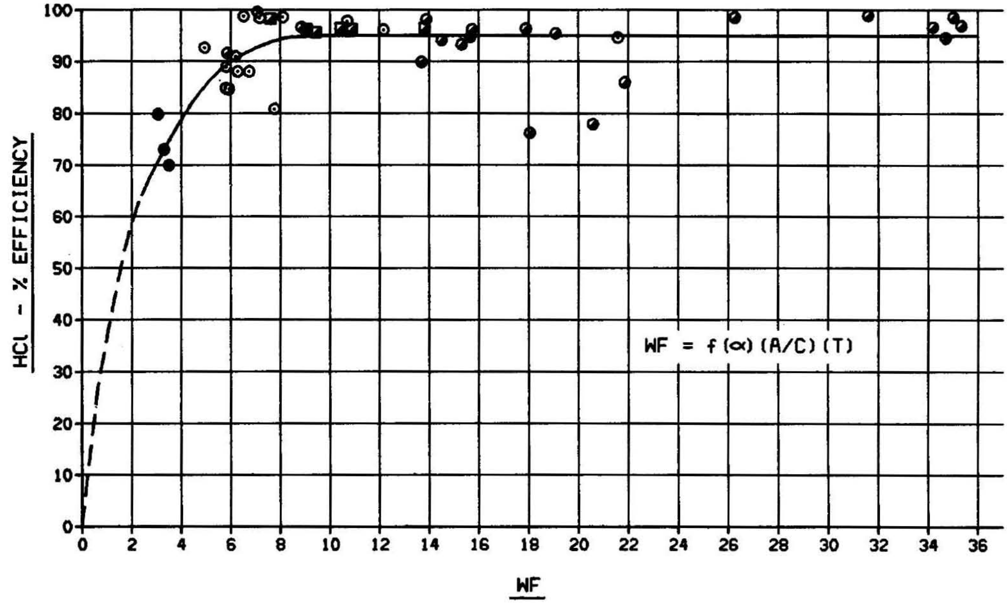

Figure 3. Baghouse efficiency—HCL Teller systems.

TABLE 3. COMPARISON OF DESIGN SPECIFICATIONS AND OPERATIONAL INLET CONDITIONS AND REAGENT FEED.

	Design	Actual
Flow		
DSCFM	42,500	41,000–48,000
ACFM	88,000–96,000	85,000–112,000
Temperature °C	204–249	215–265
H_2O Vol %	15.5	14-16
Contaminants Average		
HCl PPMDV	227	730
SO_2 PPMDV	126	213
HF PPMDV	10	20
Peak		
HCl PPMDV	605	1200
SO_2 PPMDV	205	950
HF PPMDV	20	
Particulate GM/NM^2	6.8	2.6–5.0
LIME	172	340
Average KG/H	1.6	1.5

the order of 95% have been demonstrated in this thick cake. (Figure 3). Thus, the baghouse acts as the modulator of high transient concentrations that overload the quench reactor. The behavior during transient conditions is indicated in Table 4. Thus, the efficiency will always be greater than 97.9% and will average about 99% for acid gas recovery. The thick cake also improves the particulate filtration efficiency and the dry venturi effect enhances recovery of the respiratory ingestible particulate.

The Commerce system began operation in February, 1987. After debugging, mechanical revisions, and fine tuning, the system was officially tested in May and June, 1987 by Energy Systems Associates with the approval and observation by the California Air Resources Board (CARB) and the South Coast Air Quality Management District (SCAQMD).

TABLE 4. EFFECT OF BAGHOUSE CLEANING CYCLE—8 HOURS ON ACID GAS RECOVERY.

	Efficiency %			
Acid Gas Loading Conditions	Quench Reactor	Dry Venturi	Baghouse	Overall
Low	90	30	95	99.7
Normal	80	30	95	99.3
High	40	30	95	97.9

*Based on composite data from pilot and commercial plants.

SYSTEM OPERATION

The system operation has been as follows: the flue gas is induced into the system by the system induced draft fan controlling the draft in the combustion zone. After passing through the boiler, the gas enters the quench reactor. The larger particulates, including incandescent material, is removed from the gas stream in the cyclonic inlet and the gas proceeds upward toward the multiple spray zone. The lime slurry is fed at a rate controlled by the outlet temperature from the quench reactor. The dried gas effluent from the quench reactor proceeds to the dry venturi where it is contacted by the Tesisorb entrained in ambient air. The final gas stream then proceeds to the baghouse and then through the I.D. fan to the stack. A comparison of design and operating conditions is shown in Table 3.

The system pressure drop in operation ranged from 150–250 mm w.g. compared with the design level of 250 mm w.g. The cleaning cycle for the baghouse system has been 6–8 hours compared with the design level of 8 hours. The emission control performance data are indicated in Tables 4 through 9.

Particulate

The outlet total particulate (Table 5) was reduced to 9.8 mg/Nm^3 or 0.0043 GR/DSCF (corrected to 12% CO_2). Unique in the behavior of the particle size distribution in

TABLE 5. PARTICULATE AND ACID GAS CONTROL.

	Boiler Exhaust	Teller System Outlet
Total Particulate		
mg/Nm^3	3801	7.3
Mg/Nm^3 (corr. 12% CO_2)	4602	9.8
gr/DSCF	1.65	0.0032
gr/DSCF (corr. 12% CO_2)	2.01	0.0043
Fine Particulate (<2 microns)		
mg/Nm^3		0.55
mg/Nm^3 (corr. 12% CO_2)		0.73
gr/DSCF		0.0002
gr/DSCF (corr. 12% CO_2)		0.0003
HCl		
PPMDV	731	7.15
PPMDV (corr. 3% O_2)	1152	11.35
SO_2		
PPMDV	213	0.98
PPMDV (corr. 3% O_2)	300	1.56
SO_3		
PPMDV	37	0.09
PPMDV (corr. 3% O_2)	52	0.15
HF		
PPMDV	13	0.031
PPMDV (corr. 3% O_2)	20	0.049
Heavy Metals		
PPH	6.1-7.2	<0.025*

*Inclusive of all non-detectable limits

the outlet particulate was the effective absence of the respirable sizes, 0–3 microns. It would be normally anticipated that the prepondent fraction, in an emitted particulate, would be in the respirable range because of the higher efficiency of removal of the larger particulates.

Reproducing the behavior of the Tushima-Teller system [7], the fraction of the solid particulate in the respirable range, 0–3 microns, was less than 0.1. Thus, the apparent behavior of the system is selective removal of the fine particulate where the heavy metals and the absorbed dioxin group are concentrated. A more technically acceptable explanation is that the normal operating particulate emissions are essentially zero, reflecting the 10% fine particulate present in the total particulate emission and the majority of the particulate emitted represents that discharged from the bags during cleaning. This group would consist primarily of reagent, reactants, and the larger fly-ash group.

Acid Gas Reduction

The reduction of HCl, SO_2, SO_3, and HF was generally greater than 99% (see Table 5). The average reduction, as anticipated in Table 3, of the HCl, SO_2, and HF was accomplished by neutralization in the quench reactor, dry venturi, and the accumulated reagent in the baghouse. The constant feed lime provided in an operation (ratio of lime feed to stoichiometric requirement) of 1.5 for average conditions and decreased to 0.5 during peak emissions. The SO_3 recovery occurs via sublimation to 0.3 micron mist in the quench reactor, capture by Tesisorb in the dry venturi and the final collection of the larger conglomerate in the baghouse.

Heavy Metal Control

The reduction in the non-volatile heavy metals was greater than 99.7% when the outlet quantity was based on the assumption that the non-detectable limit concentrations were actually emitted. There was no evident reduction in mercury (see Tables 6, 6A). Effective control of mercury was achieved at the Teller installation at Skovde (Sweden), where reduction to an outlet average of 11 ng/Nm^3 was achieved with inlets as high as 10,510 ng/Nm^3. The Skovde unit is an all-dry system consisting of a dry venturi and baghouse with an operating temperature of 140°C. The adsorbent fed in the dry venturi was activated carbon in addition to the silica-alumina compound and hydrated lime.

TABLE 6. HEAVY METAL CONTROL CONC. IN MG/NM^3 (CORR. 12% CO_2).

	Boiler Exhaust	Teller System Outlet
Antimony	1.6-1.9	ND (<0.034)
Arsenic	0.19-0.22	ND (<0.0020)
Beryllium	0.0066-0.0079	ND (<0.0007)
Cadmium	2.4-2.7	ND (<0.0041)
Chromium	0.64-0.74	ND (<0.0007)
Copper	5.0-5.8	ND (<0.0041)
Lead	43-51	0.0021-0.0042
Mercury*	0.040-0.046	0.27-0.58
Nickel	0.59-0.69	ND (<0.0028)
Selenium	0.015-0.017	ND (<0.0014)
Silver	0.12-0.14	ND (<0.0030)
Thallium	ND (<0.011)	ND (<0.0028)
Zinc	65-76	ND (<0.12)

*Not included in total.

TABLE 6A. MERCURY EMISSIONS DATA FROM SKOVDE INCINERATOR.

Conc. in mg/Nm^3 (Corr. 10% CO_2)

Inlet (From Boiler)	Outlet Stack
0.294	0.009
10.510	0.025
0.922	0.0065
0.514	0.0045

Hydrocarbons and Chlorinated Hydrocarbons

The hydrocarbon control targets were met with the emissions below detectable limits. The presence of

TABLE 7. CHLORINATED HYDROCARBON CONTROL.

	Boiler Exhaust	Teller System Exhaust
Di Cl Benzene	0.65	0.26
Tri Cl Benzene	1.18	0.43
Tetro Cl Benzene	0.5	0.13
Penta Cl Benzene	0.3	ND (<0.3)
Hexa Cl Benzene	ND (<0.6)	ND (<0.3)
Mono Cl Phenol	ND (<0.6)	ND (<0.3)
Di Cl Phenol	ND (<0.6)	ND (<0.3)
Tri Cl Phenol	0.5	<0.4
Tetro Cl Phenol	0.13	ND (<0.05-0.3)
Penta Cl Phenol	ND (<0.6)	ND (<0.3)
Mono Cl PCB	ND (<0.6)	ND (<0.3)
Di Cl PCB	ND (<0.6)	ND (<0.3)
Tri Cl PCB	ND (<0.6)	ND (<0.3)
Tetra Cl PCB	ND (<0.6)	ND (<0.3)
Penta Cl PCB	ND (<0.6)	ND (<0.3)
Hexa Cl PCB	ND (<0.6)	ND (<0.3)
Hepta Cl PCB	ND (<0.6)	ND (<0.3)
Octa Cl PCB	ND (<0.6)	ND (<0.3)
Nona Cl PCB	ND (<0.6)	ND (<0.3)
Deca Cl PCB	ND (<0.6)	ND (<0.3)

TABLE 8. DIOXIN—FURAN CONTROL.

	Boiler Exhaust	Teller System Exhaust
2378 TCDD	ND (<0.097)	ND (<0.003)[a]
Total TCDD	0.865	0.112
12378 Penta CDD	0.097	ND (<0.030)[a]
Total Penta CDD	0.448	0.051
Total HxCDD	1.261	<0.102[b]
Total PhCDD	2.16	0.125[c]
Total OCDD	3.47	0.225
Total PCDD	8.20	<0.61
Toxic Equiv. PCDD	<0.236	<0.009
Toxic Equiv. PCDF	1.916	<0.066

[a] Not detected in the 3 samples.
[b] Not detected in 2 of 3 samples.
[c] Not detected in 1 of 3 samples.

chlorinated aromatic hydrocarbons in the boiler exhaust gas is further indication that the dioxin precursors are present for combination on the flyash catalytic surfaces. Exclusive of the non-detectable components, the system reduced the chlorinated organics by 75% (see Tables 6, 8).

Dioxins and Furans

The dioxin and furan sampling and analysis was conducted in accordance with the sampling (CARB Modified Method 5) semi-vost consisting of a heated quartz filter followed by an XAD-2 sorbent module and by an impinger train to collect moisture and residual dioxins and furans. A full blank was collected and analyzed for all species and a 6 m^3 sample was taken for all tests over 3 to 6 hours.

The analysis was conducted by Triangle Laboratories, who prepared the resin, loaded modules, and extracted the modules. Surrogates were added to all samples. The analysis was conducted on the XAD-2 extract and the combined recovery of the probe wash, filter, connecting glassware rinse. The first impinger measurement was conducted by the GC-MS method.

Although the furnace operating conditions were within the parameters for thermal destruction of the dioxins, the concentration of the total PCDD in the boiler emissions was 8.2 ng/Nm^3 (corr. 12% CO_2). This emission level was significantly lower than the levels observed in other installations, even after collection by an electrostatic precipitator (Table 9). However it was greater than those permissible by European regulatory standards, 2 ng/Nm^3.

The reductions in the dioxin and furans achieved by the emissions control systems are shown in Table 9, indicating system outlet of 0.61 ng/Nm^3 for PCDD and 0.009 ng/Nm^3 for the dioxin toxic equivalent inclusive of nondetectable limits. The reduction of the various dioxin cogeners is indicated in Table 9. The reduction in toxic equivalents of the dioxins and furans emitted by the furnace and boiler was reduced approximately 96%.

TABLE 9. DIOXIN EMISSIONS REPORTED FOR RESOURCE RECOVERY INSTALLATIONS.

ng/Nm^3 12% CO_2

	2378 TCDD	TCDD Other	PCDD	Emission Control System
Commerce	0.003[a]	0.109	<0.615	Teller
Tulsa	0.101	1.512	18.93	ESP
Marion	0.081	0.114	1.131	Teller
Westchester	0.41	3.72	34.93	ESP
Saugus	1.7	30.2	169.2	ESP
N. Andover	1.0	12.8	114.1	ESP

[a] Not measured — used lowest detectable limit value.

TABLE 10. DIOXIN AND FURAN REDUCTION.

	Percent Reduction
2378 TCDD	96.9
Total TCDD	87.1
12378 PCDD	97.0
Total Penta CDD	88.6
Total HxCdd	>92.0
Total HpCDD	94.2
Total OCDD	93.5
Total PCDD	>93.6
Toxic Equiv. PCDD	96.2
Toxic Equiv. PCDF	>96.6

SUMMARY

The emission control system at the Commerce Resource Recovery Facility, performing with an on-line reliability of 98%, has provided a reduction in acid gas emissions in excess of 99%, with total acid gas emissions less than 15 PDMDV. It has also provided a total particulate emission of 9.9 mg/Nm^3 (corr. 12% CO_2) and a respirable dust emission less than 0.5 mg/Nm^3. The heavy metal reduction was in excess of 99.7%. The toxic equivalent of the dioxin emissions was less than 0.009 ng/Nm^3, less than 5% of the most restrictive standard established in Sweden. The concentration of hydrocarbon emissions is less than present in the ambient Los Angeles atmosphere [*10*].

NOMENCLATURE

A/C = Air to cloth ratio at baghouse
PPM = Parts per million, dry volume
PPH = Pounds per hour
T = Residence time of baghouse filter cake
WF = Moving wave front number
α = Ratio of quantity of reagent feed to the stoichiometric requirement

$$\alpha = \frac{\text{mols Ca}}{\frac{\text{mols HCl}}{2} + \text{mols SO}_2}$$

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Treatment of Hazardous Substances in Wastewater Treatment Plants

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For many types of hazardous wastes, particularly those contained in high volume, low concentration wastewaters, biological treatment in existing facilities, perhaps in selected publicly owned treatment works (POTWs), may be a better alternative. The motivation for using existing biological facilities to treat hazardous wastes is very high since there is insufficient hazardous waste treatment capacity. This problem will become exacerbated in the future unless the current hazardous waste facility problems are resolved.

INTRODUCTION

Since the passage of the PL 92-500, most municipalities in the United States have constructed some type of secondary wastewater treatment facilities. The vast majority of these use the activated sludge process to remove the organic soluble and colloidal pollutants. In this process, biodegradable material is oxidized to carbon dioxide, water, or converted to biomass. Non-biodegradable pollutants may pass through the process, but are more often removed from the liquid phase, either by adsorption onto biological flocs that are subsequently removed in secondary clarifiers or volatilization to the atmosphere during aeration.

These publicly owned treatment works (POTWs) were designed to treat municipal wastewaters comprised primarily of biodegradable materials from domestic operations, such as human wastes, kitchen wastes, and washing byproducts. Consequently, the process has been optimized for treating these easily biodegraded materials. Commercial and industrial discharges almost always have separate treatment systems. These treatment systems often discharge their effluents into POTWs, and for this reason they are actually functioning as pretreatment systems.

Municipalities like Los Angeles have many industries discharging into their treatment system. Consequently, the wastewaters are composed not only of municipal wastes but also of industrial components. The industrial contribution results from imperfect pretreatment systems, fugitive emissions, or illegal discharges. Table 1 shows

TABLE 1. SOURCES OF TOXIC COMPOUNDS.

Compound	Anthropogenic Sources	Natural Sources
Cresols	Auto Exhaust Roadway Runoff Asphalt Runoff Petroleum Distillates Oils, Lubricants	Coal Petroleum Wood Constituent Natural Runoff
Xylenols	Roadway Runoff Asphalt Runoff Fuels, Solvents Plastics Pesticides Catalytic Cracking	Coal
Isophorone	Solvent for Resins Lacquers and Finishes Pesticides Organic Chemical Mfg.	
PAHs*	Air Pollution Processing of Fossil Fuel Combustion of Fossil Fuel Roadway Runoff Catalytic Cracking	Plant and Animal Pigments Crude Oil Grass and Forest Fires

* Polycyclicaromatic hydrocarbons

potential sources for the compounds being investigated in this project.

In the current environment of increasing control of hazardous wastes, municipal plants are being evaluated for a larger treatment roll. Few economical and reliable hazardous waste treatment alternatives exist, and those that do are reserved for the most hazardous and problematic wastes. It is proposed that municipal systems be reevaluated as a treatment technology for commercially significant, "semi-hazardous" waste. Wastes that can be biodegraded or adsorbed to sludge, and those that cannot be conveniently isolated from municipal waste or urban runoff, are the best candidates for treatment in POTWs.

To evaluate the suitability of conventional plants to treat these wastes, a survey of industrially significant candidate compounds was made and several were selected for experimental investigation. A two year experimental investigation was conducted using 12 liter complete mixing biological reactors, with integral clarifiers. This paper reports our findings for a significant fraction of these compounds, representing alicyclic and aromatic compounds, using isophorone, several isomers of xylenol, and all three cresol isomers. Biodegradation rates and a model to predict volatilization are presented.

BIODEGRADATION

It is generally believed that before aromatic compounds can undergo ring-fission, the benzene nucleus must contain at least two hydroxyl groups. This usually results in the formation of a catechol, protocatechutate, or gentisate [*1*]. Chapman and co-workers [2–*4*] found that the degradation of 2,4 xylenol was initiated by the oxidation of the methyl substituent para to the hydroxyl group and that p-cresol and 3,4 xylenol were attacked in a similar manner [*5*]. The further degradation of 4-hydroxy-3-methylbenzoic acid, from 2,4 xylenol, involves oxidation of the methyl substituent to a carboxyl group forming 4-hydroxy-isophthalic acid followed by an oxidative decarboxylation of the newly formed carboxyl to give protocatechuic acid. Protocatechuic acid is then metabolized to b-ketoadipic acid by protocatechuic acid-3,4-dioxygenase. Figure 1 shows the overall pathway. In 2,4 xylenol both methyl groups undergo oxidation in succession

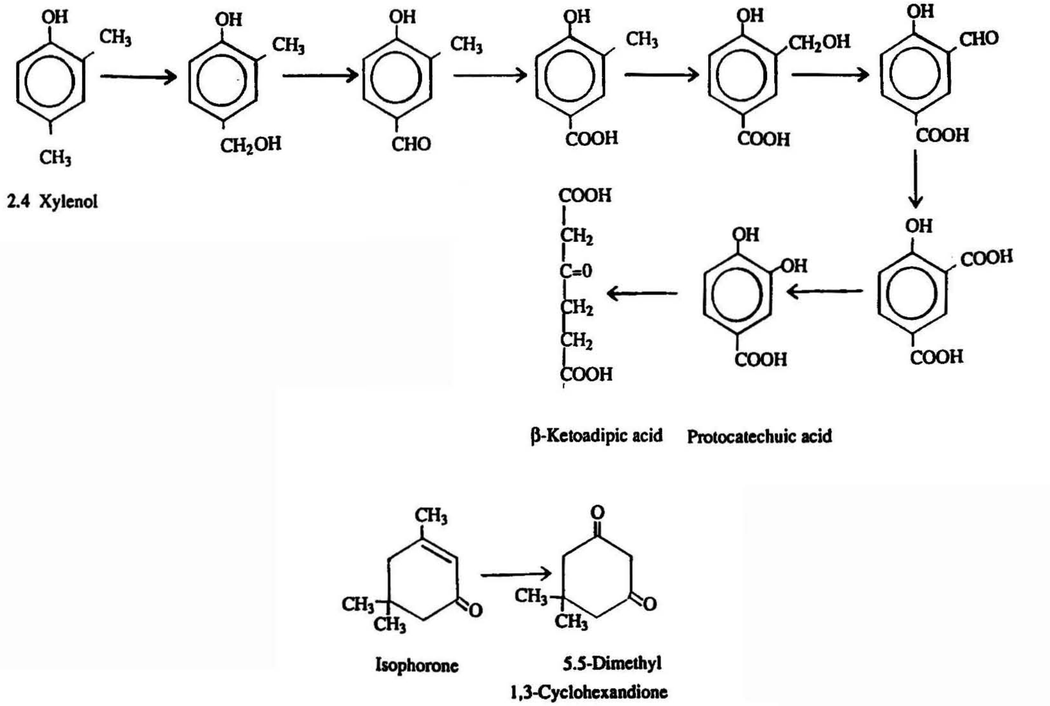

Figure 1. Biodegradation pathways for 2,4 xylenol (after Chapman (1971)) and isophorone (speculated).

with the original ortho methyl group being replaced by hydroxyl to produce protocatechuic acid. For the xylenols utilizing the pathways involving catechol and gentisate, one or both of the methyl groups remain intact until after ring cleavage. Hooper [3] showed that a species of Pseudomonas initiated the degradation of cresols and xylenols by oxidizing a methyl group placed meta to the hydroxyl group, and added a second hydroxyl group para to the first. As a result m-cresol, 2,5 xylenol, and 3,5 xylenol were oxidized to gentisic acid, 4-methylgentisic acid, and 3-methylgentisic acid, respectively. Dagley and Patel [5] found that *Pseudomonas putida* was able to utilize 2,3 xylenol and 3,4 xylenol, as well as phenol and o-, m-, p-cresol. They suggested that the catabolism of these compounds proceeded via direct ring hydroxylation and meta ring cleavage of the resulting catechols.

The pathways of the alicyclic hydrocarbons are not as well researched. Alicyclic hydrocarbons are resistant to microbial attack and microorganisms capable of utilizing them as sole carbon sources are not easily isolated. The difficulty in isolating single microorganism may arise because degradation occurs primarily under conditions of co-oxidative metabolism, and in commensal situations. Trudgill [6] achieved the best results when using mixed cultures to study the degradation of alicyclic compounds. From our results, using mass spectrophotometry, isophorone undergoes oxidation resulting in the number 3 methyl group being replaced by an oxygen. The resulting intermediate is 5,5-dimethyl-1,3-cyclohexandione. Our results show that ultimately isophorone is completely degraded.

The results presented indicate that many of these reactions are mediated by enzymes of broad specificity, inducible by structurally related compounds. Exposure of the bacteria to a single compound can induce the production of enzymes that can partially or completely metabolize a whole class of compounds. In activated sludge there is the potential for the induction of many degradation pathways. Enriching activated sludge in microorganisms that utilize a particular pathway can enhance the degradation other aromatic or alicyclic hydrocarbons that may also be degraded by that pathway.

EXPERIMENTAL METHODS

Reactor Description

Three identical continuous flow activated sludge reactors were operated in parallel and used as a source of microorganisms for experimentation. Initially, one received 2,4 xylenol, one received isophorone, and the third served as the control. All three reactors received a glucose solution, which served as the primary substrate. This feed stock, reactor geometry, and operating conditions have been described by Ng, et al. [7].

The concentrated glucose feed was prepared and automatically diluted before being pumped into the reactors. This concentrated feed was diluted 404 times resulting in influent glucose concentration of 250 mg/L. The feed solutions were refrigerated at 5°C.

The toxic compounds were pumped from separate reservoirs. The concentration of toxic compound in the reactor influent was gradually increased over time to allow acclimation of the activated sludge cells. The 2,4 xylenol solution in water was prepared at a concentration such, that when combined with the glucose feed, the maximum concentration, after acclimation was 110 mg/L. Isophorone was similarly prepared with a maximum concentraton of 118 mg/L.

The activated sludge used to initially seed the reactors was obtained from the City of Los Angeles's Hyperion Treatment facility. To increase the probability of acclimation by maintaining a diverse cell population, cells from other treatment plants in the Los Angeles area were added periodically until acclimation was achieved. The operating parameters maintained for all reactors during the period of experimentation are shown in Table 2.

TABLE 2. ACTIVATED SLUDGE OPERATING PARAMETERS (MEAN VALUES).

MCRT	13.8 days
HRT	13.8 hrs
MLVSS	20 g/L
Glucose, as BOD_5	250 mg/L
pH	7.0
DO	>3.0 mg/L
Q	24 L/day
F/M	0.2

Analytical Methods

Isophorone was concentrated using liquid/liquid extractions [8]. Three successive extractions using 5 ml of dichloromethane to 25 ml sample were made. Excess water remaining in the dichloromethane fraction was removed after extraction and removal using anhydrous sodium sulfate. The solvent was then filtered and volume was reduced using roto-evaporation.

Xylenols, cresols, and trimethylphenol were extracted using bonded phase silica sorbents. A CH (cyclohexyl) bonded phase sorbent (Bond Elute from Analytichem International, Harbor City, CA) was used. Sample pH was adjusted to 1–2, and 5% wt/vol of NaCl was added to enhance recovery. The procedure used to complete the extraction is the same as that previously described by Chladek and Marano [9].

Compounds adsorbed onto the surface of the suspended solids in the activated sludge were extracted using a modified method from Warner [10]. One hundred ml aliquots were removed from each reactor and centrifuged. After removing the supernatant 1 ml of distilled water was added to the centrifugation vial to facilitate cell removal. Using a syringe, 5 ml of cells were removed and placed in a screw top test tube. The cells were then extracted with three successive portions of dichloromethane. Each extraction involved shaking for one minute followed by a three minute centrifugation. The dichloromethane layer was removed from the bottom of the test tube using a long needle syringe. The extract was dried and concentrated as before.

The final analysis of the samples was done using GC or GC/MS. Fused silica Supelcowax 10 column was used for both isophorone and 2,4 xylenol. For isophorone the initial temperature was 90°C, increased at 8°C/min until 270°C then held at 270°C for two minutes. For xylenols, cresols, and trimethylphenol the initial temperature was 70°C, which was then increased at 8°C/min until the final temperature of 240°C was reached. The injector temperator was 250°C, the FID detector temperature was 280°C for both compounds.

Batch Assay Procedure

Batch assays to determine biodegradation rates of isophorone, xylenol, trimethylphenol, and cresol were performed with samples of activated sludge in 150 ml bottles. For each assay, 100 ml aliquots were collected from the experimental and control reactors, and placed in separate bottles. Each bottle was then centrifuged and the supernatant discarded. One hundred ml of an aqueous solution containing appropriate amounts of the compound being tested and feed solution were added to each bottle. This mixture was then incubated and aerated for the appropriate time interval. At the end of the incubation period the reaction was stopped by adding one drop (.1 ml) of a 1 + 1 H_2SO_4 solution in H_2O. The final volume was measured and in some cases adjusted to the original volume. The sample was then refrigerated until the cells could be separated from the supernatant by centrifugation. The cells or supernatant were then extracted as previously described.

For the batch assays in which 2,4 xylenol, 2,3 xylenol, and o-cresol were tested for degradability alone and combined in a mixture, 1 and 2 liter containers of activated sludge were used. For each compound tested separately, two 1 liter beakers were incubated with the appropriate amount of toxic compound and feed solution, one beaker containing acclimated activated sludge and one containing unacclimated sludge. For the mixture, 2 liter flasks were used in place of 1 liter beakers. At periodic intervals, 25 ml of sample were removed from the beaker and flasks, acidified and immediately extracted.

VOLATILIZATION

Volatilization or stripping of organics from activated sludge plants has been investigated by Roberts, et al. [*11*], and Nanking and Rittmann [*12*]. These investigators and others have estimated the volatilization rates of trace organics using oxygen as a tracer. In general this appears to be a valid approach, and the two-film model used to estimate oxygen transfer can also be used to estimate volatilization losses.

The following analysis is presented to show that volatilization rates for xylenols and isophorone are negligible for high rates of biological destruction. In the case of both compounds, adsorption to sludge particles does not occur, and has been confirmed by experimental measurements. The material balance equations for a single volatile species C, which decays at a first order rate, become

$$\frac{dC_g}{dt} = \frac{Q_g(C_{go} - C_g)}{V_g} - K_La_C\,(C^*_{g\infty} - C_l)\frac{V_l}{V_g} \qquad (1)$$

$$\frac{dC_l}{dt} = Q_l\,\frac{(C_o - C_l)}{V_l} + K_La_C\,(C^*_{g\infty} - C_l) - KC_l \qquad (2)$$

where

Q_g, Q_l = gas and liquid volumetric flow rates, respectively

C_g, C_l = gas and liquid volumetric concentration of species C

C_{go}, C_o = inlet gas and liquid phase concentrations of species C

K = first-order decay rate.

The equilibrium concentration $C^*_{g\infty}$ is calculated as

$$C^*_{g\infty} = C_g\frac{RT}{H_e}e_d \qquad (3)$$

where

H_e = Henry's Law constant $\left(\frac{\text{atm m}^3}{\text{mol}}\right)$

R = Universal gas constant, 8.206×10^{-5} $\left(\frac{\text{atm m}^3}{\text{mol °K}}\right)$

T = absolute temperature, °K

e_d = effective saturation depth, dimensionless, which accounts for the effect of hydrostatic pressure in the aeration system.

The decay parameter, K, is shown as a first-order reaction rate coefficient. In many situations it will be first-order, and in other situations it may be zero-order. Most biological modeling investigators use a saturation function to describe the decay rate. Such functions can be zero-order at high substrate concentrations and first-order at low concentrations. The rate is usually a function of active biomass concentration, often measured as volatile suspended solids concentration, or MLVSS. The reactors were modeled as first-order for this volatilization analysis, and K is considered a function of MLVSS.

The volumetric mass transfer coefficient, K_La_C, is estimated from the oxygen mass transfer coefficient, K_La_{02}. The oxygen mass transfer coefficient is generally known or can be estimated for particular conditions [*13*]. Roberts, et al. [*11*] have suggested that K_La be modeled as

$$K_La_C = \Psi\,K_La_{02} \qquad (4)$$

In clean water tests they have tabulated ranges of Ψ between 0.5 and 0.7 for a variety of 2 or 3 carbon chlorinated organic solutes. Considering this as a worst case for larger molecules, which should have lower diffusivity coefficients, is conservative and provides an upper bound for stripping estimates. The maximum transfer rate is also further reduced by contaminants in the wastewater, and is generally correlated by an empirical alpha factor, ranging from 0.2 to 0.8.

Figures 2A and 2B show the results of using the model described by Equations (1) to (4) for a typical domestic wastewater treatment plant. Figure 2A shows the losses for complete mixing reactor and Figure 2B shows the losses for a plug flow system simulated by four CSTRs in series. The aeration rate is tapered 2 to 1. The volume and size parameters were selected for a 1,000 m³/hr (6.5 MGD) treatment plant with 6-hour hydraulic retention time. The gas is also modeled as a complete mixing reac-

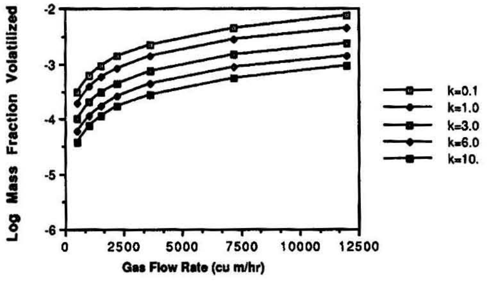

Figure 2a. Volatilization losses of 2,4 xylenol in a CSTR for varying gas flow rates.

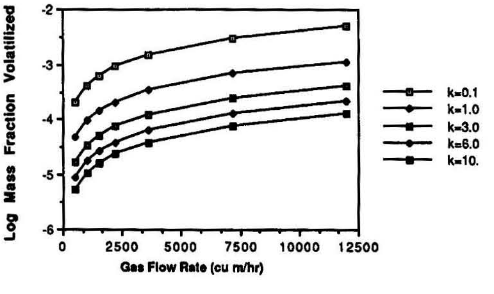

Figure 2b. Volatilization losses for 2,4 xylenol in a dispersed flow reactor (4 tanks-in-series) with tapered aeration rates.

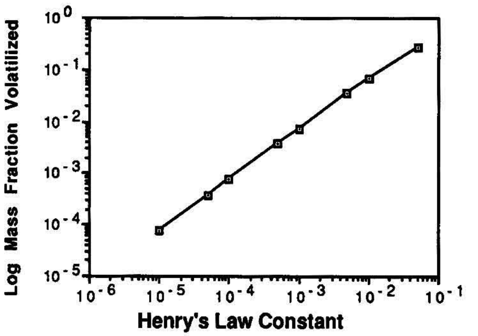

Figure 3. Volatilization losses for varying Henry's Law constant.

tion, and a hold up gas volume of 140 m^3 is typical for a subsurface aeration system in a 4.5 m (15 ft) deep tank. A typical value of K_La_{02} would be 5 hr^{-1} for a fine bubble diffused aeration system transferring approximately 7% oxygen. Gas flow rates for these conditions should be approximately 500 to 1500 m^3/hr. This represents typical operation for a modern activated sludge process system found in a municipal treatment plant. The possible range of all anticipated gas flow rates for all conceivable aeration systems is approximately 500 m^3/hr for the highest efficiency subsurface aeration system, to 12,000 m^3/hr for the lowest efficiency spiral roll system.

For the lowest K the treatment efficiency is only about 40%. At this rate approximately 0.006 mass fraction is lost by volatilization with the lowest efficiency aeration system. The typical aeration system using 1500 m^3/hr loses less than 1 × 10^{-3} mass fraction. For greater degrees of biological treatment the losses are much less, as low as 10^{-5} mass fraction. The plug flow reactor loses much more at lower biological treatment efficiencies, due to the higher per unit volume gas flow rate in the early stages. Figure 3 shows the results for a CSTR for varying Henry's Law coefficients. Volatilization losses become significant when the Henry's Law constant becomes 10^{-2} to 10^{-3}. For the compounds used in this study we expect no measurable volatilization losses. The rate of volatilization is affected by gas flow rate. Therefore high efficiency submerged aeration systems such as fine bubble diffusers should be used to minimize volatilization rates.

Biodegradation Results

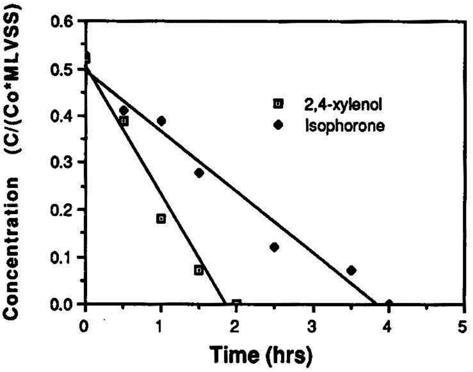

Figure 4. Time series destruction data for xylenol and isophorone, illustrating zero order rates.

Table 3 shows the results of our reactor studies for xylenols, cresols, and isophorone. Degradation rates were calculated from time series data, as shown in Figure 4. Both first-order and zero-order kinetic coefficients were calculated. Zero-order kinetics describe the experimental results better than first-order results, which should be expected in this high concentration range.

Figure 5 shows the results of an experiment designed to show that the reaction rate, while zero-order with respect to substrate concentration, is first-order with respect to MLVSS concentration. The data shown in Figure 5 were collected in batch assays. Cells were diluted with distilled water to obtain the desired concentration. Figure 5 shows the ratio concentration measured at one hour into the batch assay divided by the initial concentration. At 2.1 g/L MLVSS concentration approximately 64% of the 2,4 xylenol was destroyed after one hour. At 1.05 g/L approximately 28% was destroyed. The results indicate that the zero-order reaction rate constants tabulated in Table 3 are approximately first-order with respect to MLVSS concentration.

The continuous experiments were conducted for several months for each compound. After acclimation no detectable (<5.0 μg/L) effluent concentrations of the experimental compound were found. No stable intermediates or byproducts were observed. An intermediate was found in the isophorone batch assays, and was tentatively identified as 5,5 dimethyl-1-3-cyclohexadine. The extremely low effluent concentrations indicate that complete destruction of the compounds is possible. No experiments were performed to determine Monod half-saturation coefficients. However, they must be quite low, as indicated by the less than detectable effluent concentrations.

TABLE 3. TYPICAL RESULTS FROM A CULTURE ACCLIMATED TO 2,4 XYLENOL

Compound	Minimum Degradation Rate (Co-C)/ (MLVSS *ΔT)	MLVSS (gm/L)
2,4 xylenol	15.37	2.160
2,3 xylenol	3.04	2.240
2,5 xylenol	2.87	1.582
2,6 xylenol	0.94	1.909
3,4 xylenol	4.62	1.909
3,5 xylenol	0.00	3.102
2,4,6 trimethylphenol	2.18	1.909
o-cresol	1.49	2.518
p-cresol	1.46	2.518
m-cresol	1.47	2.518

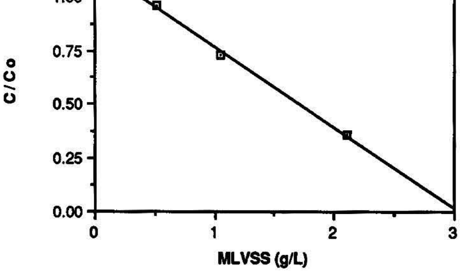

Figure 5. Xylenol concentration versus MLVSS concentration after one hour exposure.

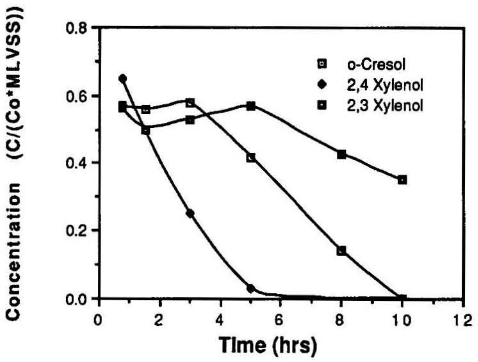

Figure 6. o-Cresol, 2,4 xylenol, and 2,3 xylenol versus time.

Figure 6 shows the results of a mixed substrate experiment using 2,4 and 2,3 xylenol and o-cresol. The culture was previously acclimated to 2,4 xylenol, which disappears first. After the disappearance of 2,4 xylenol the 2,3 xylenol and o-cresol begin to degrade.

The compounds used in the study do not adsorb onto the microbial solids. If this were to happen then their ultimate fate would depend upon sludge disposal technique. In some cases, adsorption might be desirable and in other cases it would not.

CONCLUSIONS

Previous work by Chapman [4] has shown that the degradation of 2,4 xylenol undergoes hydroxylation at the 2 and 4 position to give protocatechutate, which is then metabolized by ortho fission of the benzene nucleus. The enzymes of the first part of this reaction have been shown to have broad specificity, oxidizing 3,4 xylenol, and p-cresol. The enzymes catalyzing the remaining degradation steps in the conversion of p-hydroxybenzoic acid to b-ketoadepate possess a high degree of specificity.

Our results indicate that the mechanisms that occur in the degradation of 2,4 xylenol in pure culture can also be found in our activated sludge process enriched for 2,4 xylenol degradation. The same culture will also oxidize the other isomers of xylenol that have methyl groups in the 2 or 4 position, all isomers of cresol, and 2,4,6 trimethylphenol. All compounds that appear to degrade well with these cultures have a methyl group in the 2 or 4 position. Of these, o-cresol degrades the slowest. 3,5 xylenol did not biodegrade in any batch assay experiments, even those that lasted 14 hours.

There were no intermediates of degradation identified by gas chromatography when the test compound had reached nondetectable levels. Consequently, although the initial oxidation of the methyl group of the phenols most likely was oxidized by the enzymes provided by the cells that degrade 2,4 xylenol, the completed oxidation of the compound must involve other microorganisms. Since their numbers are much less, due to lack of enrichment, the compounds that utilize alternate pathways are degraded at a much slower rate.

Enrichment of activated sludge that contains microorganisms that utilize cometabolism and/or commensalism, as well as produce enzymes of broad specificity could be an efficient and cost effective way to degrade toxic waste. The concept here could be expanded, such that the activated sludge could be acclimated to all three pathways involving the intermediates gentistic, protocatechuic acid, and catechol by feeding it 2,4 xylenol, 2,5 xylenol and 2,3 xylenol, respectively. The resulting enriched activated sludge could then degrade, with expediency, a wide range of phenolic compounds. Figure 7 shows an enrichment factor concept whereby a small reactor treating a selected substrate, as described above, could continuously seed a large activated sludge process.

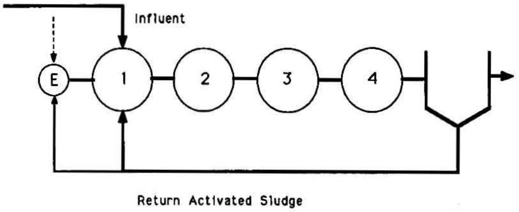

Figure 7. Activated sludge process with enrichment reactor (E).

Our modeling results show that volatilization of xylenol and compounds with similar Henry's Law constants $(\sim 10^{-5})$ is insignificant in the presence of high rates of biodegradation. Typically, mass fraction of less than 10^{-4} to 10^{-5} percent will occur with effective biodegradation. Without degradation losses increase to slightly less than 0.01 mass fraction.

ACKNOWLEDGMENTS

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Waste Treatability Tests of Spent Solvent and Other Organic Wastewaters

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Some commercial and industrial facilities treat RCRA spent solvent wastewaters by steam stripping, carbon adsorption, and/or biological processes. Thirteen facilities were visited by EPA's Office of Research and Development (ORD) from June 1985 to September 1986, to conduct sampling and analysis episodes and to determine the levels of performance achievable by these and other treatment processes. This paper summarizes the results of five of the tests: two steam strippers, two carbon adsorption systems, and one activated sludge biological system.

INTRODUCTION

Large volumes of organic chemical wastes are generated annually in the United States from manufacturing and processing operations. It was estimated that over 3 billion gallons of spent solvents and 24 million gallons of non-solvent halogenated wastes were generated in 1981 [*1*]. The solvent wastes were among the first hazardous waste categories to be addressed in the Hazardous and Solid Waste Amendments (HSWA) of 1984. As a result of HSWA, the Environmental Protection Agency (EPA) has studied treatment technologies that can destroy or remove toxic constituents from hazardous wastes, or immobilize them prior to land disposal.

EPA collected data from available sources on the treatability of wastes containing the F001–F005 spent solvent constituents (see Table 1) [2]. Sources of treatment performance data included the organic chemicals, plastics, and synthetics fibers industries data base, the pharmaceuticals industry data base, the iron and steel manufacturing point source category data base, and numerous literature resources. To supplement the historical treatment data, EPA conducted sampling episodes for organic wastes containing the constituents of F001–F005, and transferred other data based on similarity of chemical structures.

Some of the spent solvent treatability tests involved sampling waste treatment processes at commercial treatment, storage, and disposal facilities (TSDFs) and chemical production facilities. Preference was given to sampling from on-site treatment facilities where the waste of interest is treated alone or as a major component of the total waste handled. If such on-site facilities could not be identified, the second choice was commercial facilities where mixing of many wastes is generally practiced but where extensive optimization of treatment may have occurred. Where no suitable TSDF facilities are identified, in-house tests would be conducted. Eight types of waste treatment processes were sampled at thirteen commercial-scale facilities under this program. The raw wastes, treated effluents and residues were analyzed for volatile and non-volatile organics and other constituents. The eight processes included were:

- Distillation
- Agitated Thin Film Evaporation
- Screw Auger Evaporation
- Incineration
- Waste Blending/Fuel Substitution
- Steam Stripping
- Activated Sludge
- Carbon Adsorption

The data from the facilities tested are summarized in a report, which can be obtained through the National Technical Information Service [2].

The subsequent discussions concern the treatment technologies for spent solvent wastewaters (streams containing less than one percent total organic carbon) and the results of sampling conducted at five of the thirteen facilities. These technologies are steam stripping (two sites), activated sludge (one site), and carbon adsorption (two sites).

STEAM STRIPPING

Steam stripping is a continuous fractional distillation process in which live steam is injected directly into the bottom of a packed or tray tower to strip volatile organic compounds from aqueous wastes in multiple equilibrium stages. Steam stripping is most effective in treating

TABLE 1. SPENT SOLVENT WASTES

Industry and EPA hazardous waste No.	Waste Description
Generic:	
F001	The following spent halogenated solvents used in degreasing: trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons; all spent solvent mixtures/blends used in degreasing containing, before use, a total of 10% or more (by volume) of one or more of the above halogenated solvents or those solvents listed in F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.
F002	The following spend halogenated solvents: Tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, orthodichlorobenzene, trichlorofluoromethane, and 1,1,2-trichloroethane; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above halogenated solvents or those listed in F001, F004, or F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.
F003	The following spend non-halogenated solvents: Xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone, and methanol; all spent solvent mixtures/blends containing, before use, only the above spent non-halogenated solvents; and all spent solvent mixtures/blends containing, before use, one or more of the above non-halogenated solvents, and, a total of 10% or more (by volume) of one or more of those solvents listed in F001, F002, F004, and F005; and still bottoms from the recovery of these spend solvents and spent solvent mixtures.
F004	The following spent non-halogenated solvents: Cresols and cresylic acid, and nitrobenzene; all spent solvent mixtures/blends containing, before use, a total of 10% or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed in F001, F002, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.
F005	The following spent non-halogenated solvents: Toluene, methyl ethyl ketone, carbon disulfide, isobutanol, pyridine, benzene, 2-ethoxyethanol, and 2-nitropropane; all spent solvent mixtures/blends containing, before use, a total of 10% or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed in F001, F002, or F004; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.

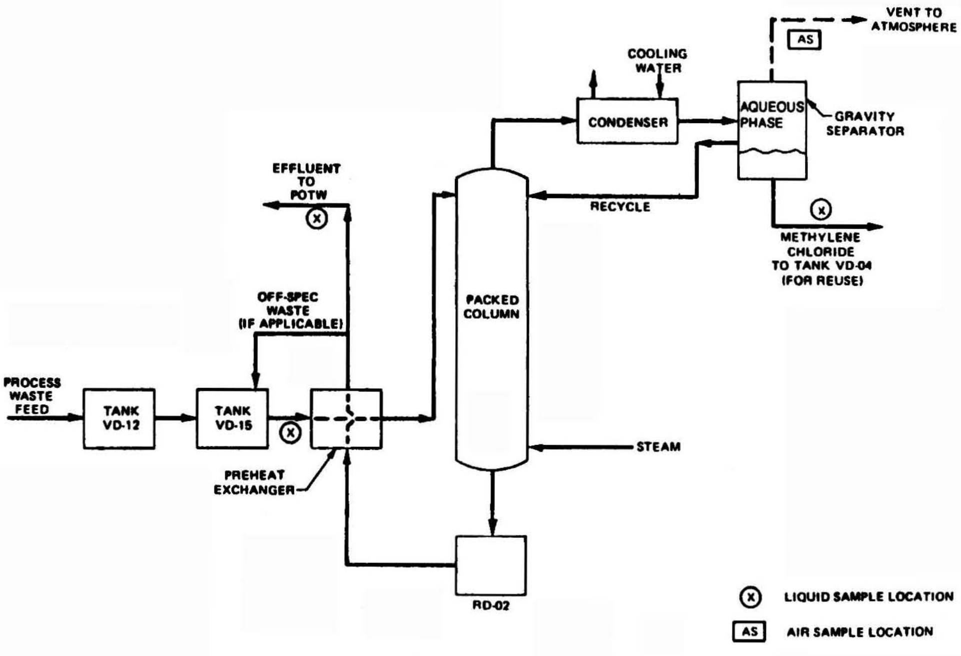

Figure 1. Facility G—methylene chloride steam stripping schematic.

TABLE 2. FACILITY G—STEAM STRIPPER ANALYTICAL DATA

	Process Waste Influent		Bottoms Effluent		Overhead Condensate Organic Phase				
Compound	Flow Rate (kg/hr)[a]	Concentration (mg/kg)	Flow Rate (kg/hr)[b]	Concentration (mg/kg)	Flow Rate (kg/hr)	Concentration (mg/kg)	Removal[d] (wt. %)	Flow Rate (kg/hr)	Concentration (mg/kg)
Methylene Chloride	4.5	3,600	$<2.6 \times 10^{-4}$	<0.19	0.088	5,110	>99.99[c]	0.095	24.7
Chloroform	0.066	52	0.0072	5.3	0.019	1,080	89	0.046	12.0
Carbon Tetrachloride	2.9×10^{-3}	<2.3	$<2.26 \times 10^{-4}$	<0.17	—	—	>92[c]	$<2.3 \times 10^{-4}$	0.06
Total Volatile Organics	4.6	3,654	7.69×10^{-3}	<5.66	0.107	6,200	>99.8	0.141	36.8
Water	1,255[e]	—	1,360[e]	—	16.9[e]	—	—	4.14	—
Total	1,260	—	1,360	—	17.0	—	—	4.28	—
Additional Parameters									
Volumetric Flows (1/min)	19.7		21.8		0.285			64.3	
Specific Gravity	1.069		1.0425		1.0167			—	

[a] Calculation: Concentration (mg/l) × Overall Flow Rate (1/hr) × 10^{-6} = kg/hr.

[b] Calculated from material and energy balances using measured flow.

[c] Outlet component concentration is below detection limit, therefore, the percent removal is calculated using the detection limit as the measured concentration.

[d] Calculated as: [1-(Effluent from Stripper)/(influent to Stripper)] × 100%.

[e] Balance of total flow after accounting for organics.

aqueous wastes containing organic compounds with low boiling points, which are relatively immiscible in water. Miscible organics such as ketones or alcohols are not as readily steam stripped. Waste streams with high concentrations of suspended solids, dissolved metals, oil, and grease may require pretreatment steps before steam stripping.

Two facilities using steam stripping to treat constituents of F001–F005 were tested. Facility G is a chemical manufacturing plant that produces a number of intermediate products used by the chemical, cosmetics, and agricultural industries. The spent solvent is methylene chloride. Facility N produces mono-carbon chlorinated solvents such as methylene chloride, chloroform and carbon tetrachloride. Their steam strippers treat an aqueous waste stream consisting of equipment washwater and rainfall collected from diked areas around the plant.

At Facility G, the process waste feed (5 gallons per minute average) to the steam stripper consisted of about 0.4% methylene chloride in water. Figure 1 illustrates their steam stripping process. The packed column has approximately five theoretical stages and was operated at approximately 101°C. Table 2 summarizes the data obtained from sampling at Facility G. The overall reduction of methylene chloride in the feed was over 99.99%. The process was less effective for chloroform (89%) and car-

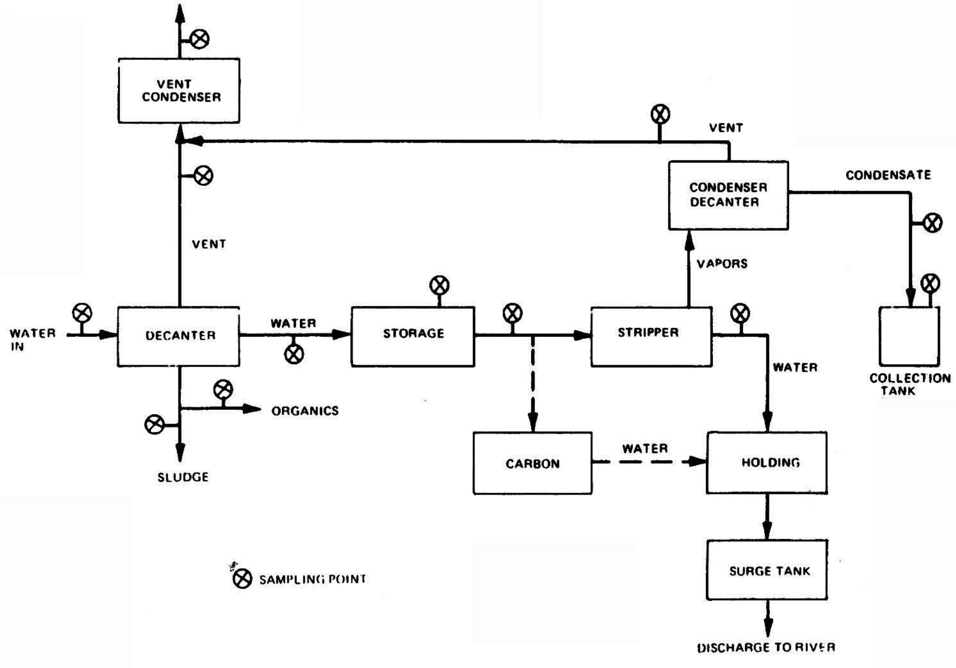

Figure 2. Facility N—steam stripping schematic and sampling points.

TABLE 3. FACILITY N—STEAM STRIPPING ANALYTICAL DATA

	Stripper	Influent	Stripper	Effluent	Organic Condensate[b]			
Compound	Flow (kg/hr)[a]	Conc. (mg/kg)	Flow (kg/hr)	Conc. (mg/kg)	Flow (kg/hr)	Conc. (mg/l)	Percent Removal (wt. %)	Primary Condenser Vent Flow (kg/hr)
Chloromethane	0.0796	33	$<1.35 \times 10^{-5}$	<0.005	—	—	>99.98[c]	0.0086
Methylene Chloride	10.96	4,490	$<2.88 \times 10^{-5}$	<0.011	9.42	1,180,000	>99.999[c]	1.05
Chloroform	3.19	1,270	$<1.67 \times 10^{-5}$	<0.006	2.78	319,000	>99.999[c]	0.160
Carbon Tetrachloride	0.316	55	$<1.35 \times 10^{-5}$	<0.005	—	—	>99.99[c]	0.014
Trichloroethylene	.028	5.6	$<1.35 \times 10^{-5}$	<0.005	—	—	>99.9[c]	—
1,1.2-Trichloroethane	.013	5.3	$<1.35 \times 10^{-5}$	<0.005	—	—	>99.9[c]	—
Total Volatile Organics	14.6	5,860	$<9.95 \times 10^{-5}$	<0.037	12.2	1,499,000	>99.999[c]	1.23
Water	2,425	—	2,680	—	—	—	—	0.013
Additional Parameters								
Flow Rates (1/min)	40.7	—	44.7	—	0.14	—	—	57
Specific Gravity	1.0	—	1.0	—	—	—	—	—

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[a] Calculation [Concentration (mg/l) + (1.069 kg/l)] × Flow Rate (l/hr) (10^{-6}) = kg/hr.

[b] Condensate rate estimated from organics in with feed minus organics out with uncondensed vapor and bottoms.

[c] Outlet component concentration is below detection limit, therefore, the percent removed is calculated using the detection limit as the measured concentration.

[d] Calculated as: (1-(Effluent from Stripper)/(influent to Stripper)) × 100%.

bon tetrachloride (92%). The bottoms from the steam stripper are discharged to the local sanitary sewer.

Figure 2 illustrates the steam stripping process at Facility N and Table 3 summarizes the data obtained. The influent flow was about 11 gallons per minute (41 liters per minute). On an average basis, methylene chloride, chloroform and carbon tetrachloride removals were all over 99.98%. The stripper bottoms are discharged to a nearby river under current NPDES permit restrictions.

The two steam stripping systems were effective at reducing the volatile organic components in the waste streams, and in recovery of spent solvents.

ACTIVATED SLUDGE

Typical activated sludge treatment processes metabolize many dissolved compounds by biologically catalyzed oxidation to carbon dioxide, water, and biomass. The process generally begins with primary treatment (equalization, screening, sedimentation), then the influent wastewater is pumped to a basin or tank where aerobic microorganisms are suspended. Effluent from the basin goes to a clarifier for settling of biological sludge. A portion of this sludge is returned to the aeration basin to maintain an optimum biomass concentration in the sys-

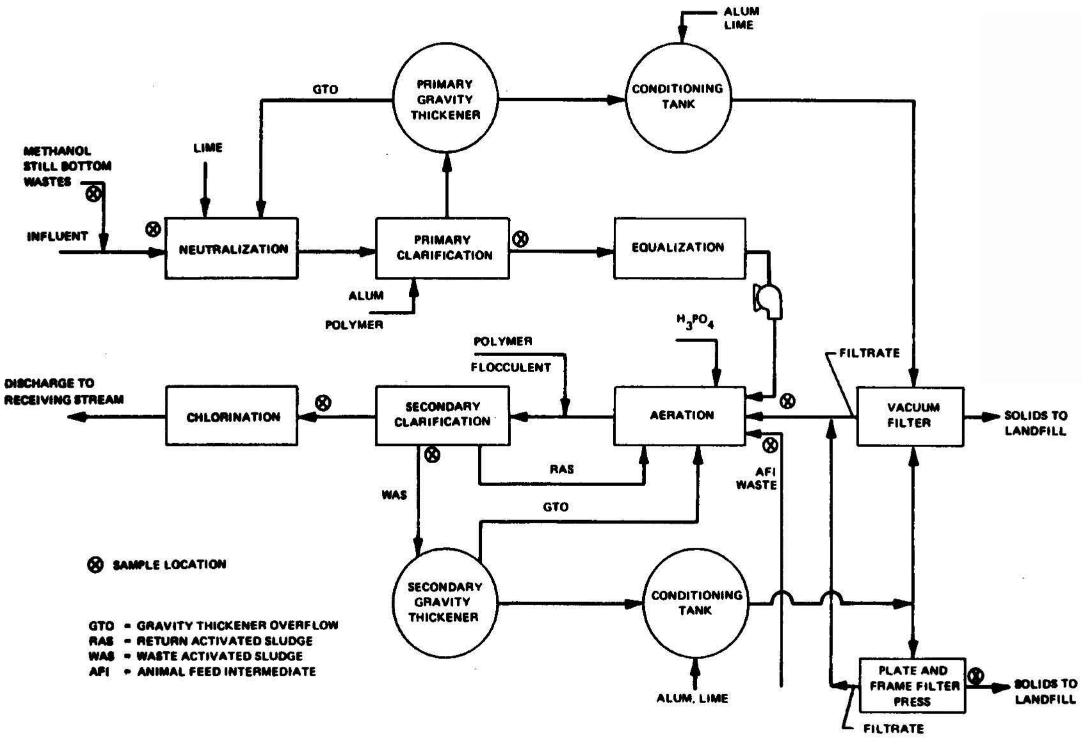

Figure 3. Biological wastewater treatment plant facility 1.

TABLE 4. FACILITY I—ACTIVATED SLUDGE ANALYTICAL DATA

Pollutant	Units	Calc. Average Meth. Still Bottoms	Calc. Average Influent to Aeration	Calc. Average AFI⁺ Influent	Calc. Average Secondary Effluent	Calc. Average Waste Act. Sludge
VOLATILE ORGANIC COMPOUNDS						
methylene chloride	μg/l	7.3	84	40	33	537*
acetone (2-propanone)	μg/l	19	774	<113	49	84*
2-butanone (MEK)	μg/l	<10	131	<35	47	22*
4-methyl-2-pentanone	μg/l	<10	2,557	<34	47	15*
toluene	μg/l	<5	1,459	<18	24	<5*
chlorobenzene	μg/l	<5	540	<18	24	<5*
methanol	μg/l	697,778	56,667	<10,000	<10,000	<10,000*
SEMI-VOLATILE ORGANIC COMPOUNDS						
2-chlorophenol	μg/l	75	22	<22	22	55*
METALS						
zinc	mg/kg	5.1	39	<13	17	1033*
OTHER ANALYSES						
BOD5	mg/l BOD	525	120	1,396	9.8	
TOC	mg/l	4198	99	1040	13	
oil & grease	mg/l	2174	28	443	55	
pH	pH units	4.4	5.9	8.3	6.4	6.5

* = Units are μg/kg.
\+ AFI = Animal Feed Intermediate.
Analyte concentrations below detection limits were considered at the detection limit for calculations of averages.

tem. Nutrients may be added to the basin for optimum biological activity. Mixing and aeration are provided for the oxidation reactions.

Facility I manufactures plastic adhesives, ultraviolet light absorbers, surfactants, and animal feed intermediate (AFI). The waste stream of interest is the bottom waters from a continuous methanol recovery stripper. This stream is mixed with wastewaters from the other processes and treated by a 3.5 million gallon per day capacity three-day hydraulic residence activated sludge plant (Figure 3). The methanol waste stream constituted about 0.1% of the influent flow and contained about 0.05% methanol. Table 4 summarizes the analytical data obtained from the testing. Methanol concentrations in nine still bottom grab samples collected during the three-day sampling program ranged from 350 to 1,600 mg/l. The average concentration was about 700 mg/l. Apparent methanol removals by the biological treatment system

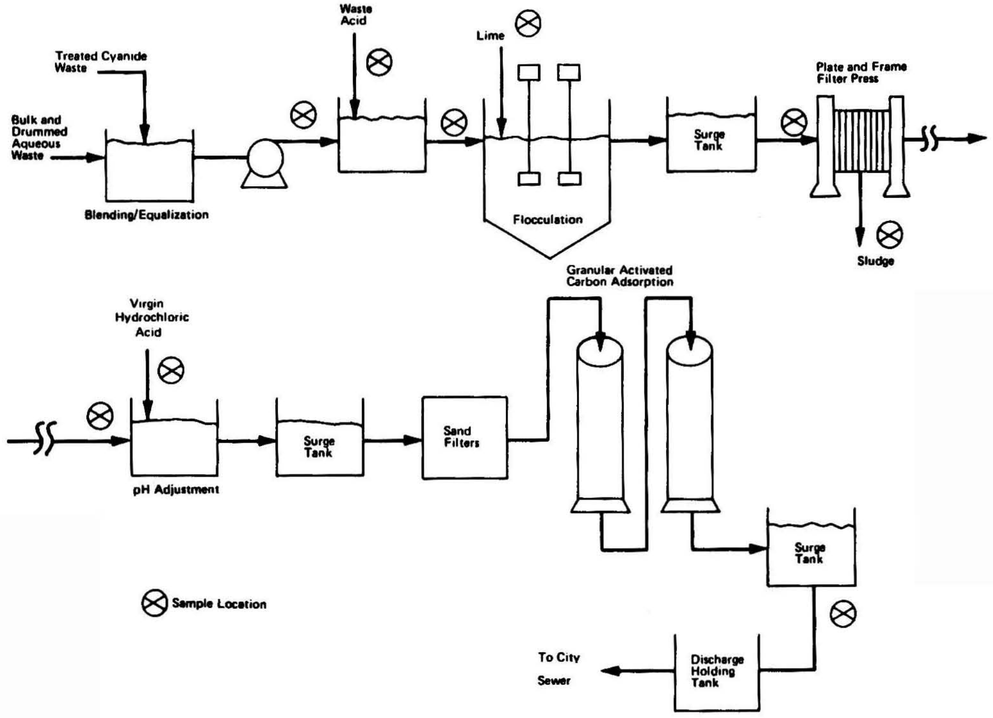

Figure 4. Facility B flow diagram/sample points for aqueous waste treatment system.

TABLE 5. FACILITY B—CARBON ADSORPTION DATA

Parameter	Units	Day 1 Filtrate	Day 1 GAC Effluent	Day 2 Filtrate	Day 2 GAC Effluent	Day 3 Filtrate	Day 3 GAC Effluent
VOC							
Methylene chloride	μg/L	220,000	<1,250	43,000	<2,500	130,000	30,000
Acetone	μg/L	68,000	140,000	61,000	160,000	69,000	55,000
2-butanone (MEK)	μg/L	<5,000	<2,500	6,600	<5,000	7,000	<5,000
1,1,1-trichloroethane	μg/L	ND	ND	2,500	<1,000	1,600	1,600
Trichloroethene	μg/L	4,200	<500	1,400	<1,000	<1,000	<1,000
Toluene	μg/L	13,000	<500	7,700	<1,000	3,900	<1,000
Total xylenes	μg/L	<1,000	<500	8,000	<1,000	<1,000	<1,000
Acid Extractables							
P-chloro-m-cresol	μg/L	5,600	<100	1,600	<100	<500	<100
2-nitrophenol	μg/L	1,200	<100	1,600	<100	3,000	<100
4-nitrophenol	μg/L	1,100	<100	2,300	<100	1,400	<100
2,4-dinitrophenol	μg/L	120	<100	<400	<100	ND	ND
Phenol	μg/L	19,000	<100	4,200	<100	5,100	<100
Base/Neutral Extractables							
N-nitrosodimethylamine	μg/L	100	<100	ND	ND	ND	ND
Metals							
Cadmium	mg/L	1.2	0.15	7.9	0.51	50	1.4
Hex. chromium	mg/L	NS	<20	NS	<5	NS	<5
Total chromium	mg/L	2.1	0.091	1.9	0.12	0.068	0.091
Copper	mg/L	160	0.32	170	0.87	380	0.56
Lead	mg/L	1.4	0.56	0.82	0.74	0.67	0.63
Nickel	mg/L	2.2	2.2	2.3	2.0	22	1.8
Zinc	mg/L	24	1.4	16	1.6	46	0.70

ND = Not determined
NS = Not Sampled

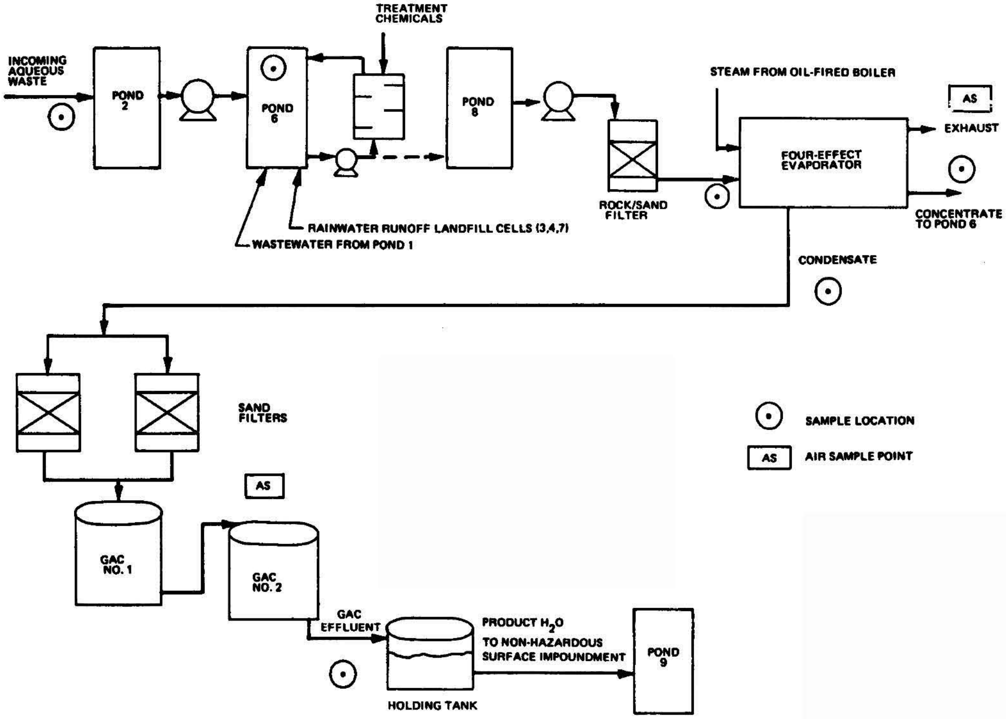

Figure 5. Flow diagram/sample points for aqueous waste treatment at facility C.

TABLE 6. FACILITY C—CARBON ADSORPTION DATA

Parameter	Units	Day 1 Evaporator Condensate	Day 1 GAC Effluent	Day 2 Evaporator Condensate	Day 2 GAC Effluent	Day 3 Evaporator Condensate	Day 3 GAC Effluent
VOC							
Methylene chloride	μg/L	34	<5	<5	<5	15	<5
Acetone	μg/L	710	<50	800	<50	850	<50
2-Butanone (MEK)	μg/L	<50	<10	360	<10	230	<10
1,1,1-trichloroethane	μg/L	<10	<2	<10	<10	34	<2
Trichloroethene	μg/L	<10	<2	<2	<2	7.5	<2
Benzene	μg/L	<10	<2	ND	ND	21	<2
4-methyl-2-pentanone	μg/L	<50	<10	26	<10	31	<10
Tetrachloroethene	μg/L	<10	<2	<2	<2	6.5	<2
Toluene	μg/L	<10	<2	9	<2	62	<2
Ethyl benzene	μg/L	<10	<2	<2	<2	5.5	<2
Total xylenes	μg/L	<10	<2	<2	<2	26	<2
Acid Extractables							
2,4-dichlorophenol	μg/L	ND	ND	37	<20	ND	ND
2-nitrophenol	μg/L	222	<20	75	<20	ND	ND
Base/Neutral Extractables							
Bis (2-chloroethyl) ether	μg/L	86	<20	<20	<20	ND	ND
Diethyl phthalate	μg/L	547	<20	<20	<20	<10	<10
isophorone	μg/L	ND	ND	21	<20	26	<10
Metals							
Zinc	mg/L	.0053	.027	<.005	<.005	.016	.013

ND = Not Determined

ranged from over 64% to over 94%. The analytical method detection limit of 10 mg/l precluded a more accurate determination of removal efficiency. Total organic carbon (TOC) and biochemical oxidation demand (BOD) removals were 85 and 94% respectively.

CARBON ADSORPTION

Activated carbon is used for removal of dissolved organic compounds from aqueous wastes. Organic molecules are attracted to the surface and pores of the activated carbon by physical and/or chemical forces. The effectiveness of activated carbon for adsorption is related to its large surface area. Surface area of typical activated carbons can range from 500 to 1,400 square meters per gram of material. In a typical fixed-bed adsorption system, wastewater flows through a vessel or bed filled with granular activated carbon, at rates from 2 to 5 gallons per minute per square foot. Flow continues until a specific volume has been treated or until one of the wastewater constituents exceeds a predetermined concentration in the bed effluent (breakthrough). At this point, the bed is taken out of service and the carbon is either discarded or regenerated offsite in a special furnace. Adsorption is most effective when the organic compounds to be removed have relatively high molecular weights, high boiling points, low aqueous solubilities, and low polarity.

Carbon adsorption was the final treatment operation in the aqueous waste treatment processes at two commercial TSDFs, Facility B and C. In both cases, granular activated carbon was used to remove dissolved organics after upstream operations removed metals and suspended solids.

Unit processes for treatment of aqueous wastes at Facility B include pH adjustment, chemical reduction, precipitation of metals, filtration, and carbon adsorption. The principal organic compounds measured in the influent were methylene chloride, acetone, toluene, nitropropane, and phenol. The waste treatment system is shown in Figure 4.

Phenol is used as an indicator for carbon breakthrough by Plant B. This is noted by a significant increase in the effluent concentration, generally about 5 to 10% of the influent concentration. Facility B's sewer discharge permit limitation for phenol is 6.16 mg/l. The phenol breakthrough normally occurs after about 20 to 25 days of operation, according to plant personnel. Table 5 summarizes analytical data for Facility B's carbon adsorption process. The total organic carbon removal averaged 90%. The phenol removal was 97%. The lower molecular weight organics (methylene chloride, acetone) were removed to a lesser degree.

Facility C's treatment of aqueous wastes included pH adjustment, precipitation of metals, filtration, and multiple-effect evaporation. Figure 5 is the flow diagram of the entire waste treatment process. The carbon adsorption system was used to further reduce the organic content of the wastewater. As shown in Table 6, the primary organic compounds in the adsorber influent were acetone and methyl ethyl ketone. The total organic carbon was reduced by 98% in C's adsorption operation.

CONCLUSION

In general, all three treatment techniques effectively removed specific volatile organic compounds to low residual concentrations. The summaries presented in this paper and the cited references may be of interest to those seeking data on the treatability of similar organic wastewaters. Each of the five case studies are discussed in greater detail elsewhere [2].

LITERATURE CITED

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2. Field Measurements of Full-Scale Hazardous Waste Treatment Facilities—Organic Solvent Wastes, EPA report, October 1988. NTIS No. (PB89-138853)

Biotreatment of Dilute Contaminated Ground Water Using an Immobilized Microbe Packed Bed Reactor

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A biological treatment process employing immobilized microbial populations was field tested on contaminated ground water having dilute concentrations of volatile organics and organic pesticides. The process, consisting of two packed bed reactors in series containing specific adapted microbial strains immobilized on a porous diatomaceous earth support, was operated in a plug flow configuration over a 90-day period at a flow rate of 80 gallons per day (gpd). Process viability of this multiple microbe/multiple toxicant treatment approach was determined based upon comparisons to carbon adsorption technology.

INTRODUCTION

The presence of dilute concentrations of known xenobiotics and/or listed chemicals in ground water is of concern from two general perspectives: first, in terms of the potential health effects consequences of this toxicant presence; and, second, from a perspective of the inordinate high costs associated with remediation of the problem. An example of the complexity of the problem is evident in the high concentrations of pesticides and related agricultural source chemicals in many communities in midwestern and southern states [*1*]. Organophosphates and organochlorines have been found in ground water in many sites and comprise tens or hundreds of thousands of acre-feet of polluted water [2].

The technology presented here focuses on the engineering aspects of cost effectively treating significant concentrations of contaminated ground water on a continuous basis. This technology, an immobilized microbe bioreactor system, is based on the principle that natural populations of microorganisms may be promoted/adapted to decompose refractory molecules. Few applications have focused on hazardous waste effluent/ground water biotreatment in which multiple microbial assemblages have been immobilized to effect biotreatment. Data are presented on initial investigations into effectively treating chlorinated hydrocarbons and organophosphates in a ground water source using an immobilized bacteria approach for above ground treatment. A field demonstration study was conducted at a pesticide formulation plant located in the continental United States.

Data have been presented elsewhere on the initial pilot tests at this site wherein basic design criteria for reactor operation was established [3]. The objectives of this phase of a multi-tiered laboratory/field investigation were to determine whether biological treatment or a combination of biological/physical-chemical treatments would be effective for the targeted ground water at dilute concentrations; to generate a simulated effluent to meet state and local permit requirements; and to obtain estimates of the configuration and size of the treatment facility and provide a cost estimate of the system involved.

MATERIAL AND METHODS

Isolation of Microorganisms

The microorganisms isolated and adapted for continuous degradation of industrial effluents are discussed in detail elsewhere [*4*]. These strains were developed for detoxification of specific industrial streams using aquatic microcosm systems (developed in earlier research efforts for the Environmental Protection Agency to analyze the environmental fate and effect of selected contaminants in coastal delta wetlands). The organochlorine degraders are selected *Acinetobacter sp* (Strains LSU 101/A and LSU 104/C). The organophosphate degraders are selected Flavobacterium sp (Strains LSU 201/F and LSU 216/F).

The growing media contained 0.5 grams of $(NH_4)_2SO_4$, 0.5 grams of $MgSO_4$, 1.0 gram of yeast nitrogen base, 20 ml of nutrient broth, Difco Laboratories, 0.5 grams of KH_2PO_4, 0.1 gram of $MgSO_2$, and 250 ml of contaminated ground water containing approximately 500 ppb toxicant. Twelve flasks, six 500 ml Erlenmeyer flasks each for organochlorines and organophosphates containing the aforementioned microorganisms and the growth media, were placed in a rotary shaker (150 oscillations per minute, 37°C.) for a period of 96 hours. Heat lamps were used to maintain temperatures. ATP assays were conducted periodically to monitor growth.

Microbe Immobilization

Bacterial strains were immobilized on the solid supports mentioned following guidelines, as described by Messing, *et al.* [*5*] and Portier and Fujisaki [*6*]. Adsorption or covalent bonding to supports (Manville, R630) is the primary mechanism for immobilization. Microorganisms are continuously introduced and recycled through the reactor module for 24 hours by a peristaltic pump to initiate viable cell attachment. Cell loading optimum (gram wet cells per liter wet catalyst) was determined using microbial ATP approaches [*7*].

Chromatographic Analysis

Gas chromatography approaches routinely used to determine the kinetic efficiency (biotransformation) by the immobilized microbial population of targeted toxicants followed methods previously outlined [*8*]. An integrated analytical procedure for organochlorine contaminants was used for the determination of toxaphene, chlordane components, and other residual organophosphate constituents found in the ground water samples. Due to the recognized volume of toxaphene associated with the ground water, this organochlorine contaminant was most carefully analyzed and served as an indicator toxicant. Toxaphene standards were used with appropriate QA/QC protocols. Additionally, preliminary evaluations of the presence of organophosphate and chlordane peaks were noted. However, due to the time restraints, an extensive characterization and quantitation of control and treated concentrations of these materials was not made. Again, our focus was on the removal of the major constituents in ground water by physical-chemical processes coupled to a microbiological approach.

The capillary column gas chromatography protocol used in these investigations was specifically designed to yield results within 1% of spiked concentrations. Additionally, the procedure allows for a careful differentiation of chlordane components from toxaphene components in ground water samples. Toxaphene is a multicomponent residue that when analyzed by conventional column gas chromatography with electron capture detection (GC/ECD) yields chromatograms containing peaks that overlap those of other organochlorine contaminants, including chlordane related components, PCBs, and homologs. Considerable effort was required to provide sufficient characterization of toxaphene constituents in the ground water to minimize the possibility of chlordane component overlap. The gas chromatography protocol developed is accurate and reproducible and enabled evaluation of the extent and magnitude necessary for interpretation of physical-chemical and microbiological processes outlined. The instrumentation used in these investigations was a Hewlett-Packard 5890 using a DV5 capillary column, and an ECD (NI/63). A methylene chloride/hexane solution (15%–85%) was used for extraction of primary chemical constituents in the ground water using analytical procedures previously developed [*8*]. The detection limit for toxaphene, the primary contaminant evaluated in the targeted ground water samples, is 3.0 ppb.

Hydrogeology Ground Water Withdrawal and Site Containment

Ground water feeding the biotreatment facility was pumped from a sand and gravel aquifer occurring 8 m in depth below ground surface (see Figure 1). The stratigraphy of the site can first be characterized as an upper stratum consisting of 4 m of low permeability clay. This stratum is unsaturated and occurs above the static water table and constitutes the vadose zone. A second underlying stratum consists of saturated silty and sandy clays averaging 3 m in thickness. The third stratum is the aquifer and can be characterized as a porous and permeable sand and gravel deposit that averages three feet in thickness. These deposits are alluvial in origin and are underlain by a thick impermeable shale, the fourth stratum, that provides a vertical barrier to ground water flow (aquiclude).

Static water level occurs at 4.2 m below ground surface. Ground water pump tests have determined the horizontal flow velocity to be relatively slow, i.e., <6.0 m/yr. Ground water was pumped from a 0.2 m diameter monitoring well utilizing a pneumatic-discharge/gravity-fill pump. Pumping was continuous whereby the daily withdrawal rates were slightly greater than the demand by the pilot plant.

While vertical ground water flow was prevented by the shale aquiclude and horizontal flow was slight, a containment structure will be installed in the near future for pur-

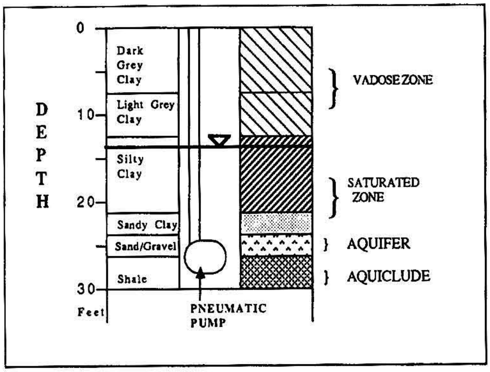

Figure 1. Site stratigraphy and groundwater withdrawal system.

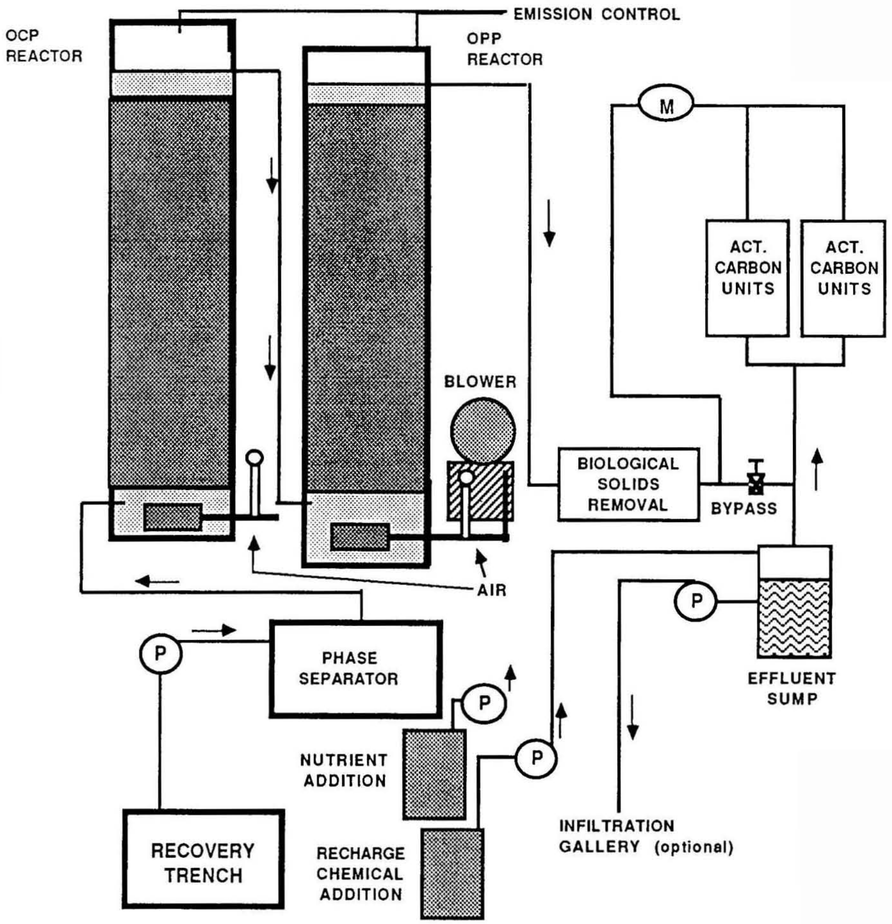

Figure 2. Treatment schematic of field pilot system.

poses of managing lateral flow and ground water level. A slurry backfilled cutoff wall consisting of low permeability materials will also be installed around the perimeter defining the area of contaminated ground water.

Biotreatment Systems: General Experimental Design

The field pilot system consisted of a series of biological treatment columns or modules with a flow capacity of 0.3 m^3/d per unit. The system consisted of a feed tank with a 19 m^3 capacity, a feed pump with a maximum 0.6 m^3/d capacity, and two biological towers, in series. The first reactor, designated OCP, consisted of a 2.0 m^3 unit approximately 3.6 m. high containing 5.4 cu. ft. of packing consisting of carrier (Celite™ R-630) provided by Manville Corporation. The unit operated in a plug flow mode with the media flooded and with a maximum aeration rate of 0.5 m^3/h.

The second biological reactor, designated OPP for organophosphate biotreatment, also was configured as a plug flow reactor containing fine bubble diffusion with a maximum aeration of 0.5 m^3/h. The unit was packed with 0.1 m^3 of carrier (Celite™ R-630) provided by Manville Corporation. A carbon post-treatment unit was placed in service should post biological toxaphene levels exceed 70 μg/L. This unit consisted of a small carbon column with approximately 0.19 cu. ft. capacity. This additional carbon column served essentially as a polishing unit.

At initial start-up, the clarified contaminated ground water was pumped directly into the biological reactors at a rate of 0.3 m^3/d. This was later increased to a rate of 0.6 m^3/d gpd total per tower. Aeration rates were maintained at 0.4 m^3/h per tower (saturation levels for both units).

Sample were obtained at four locations. The first location was the feed into the treatment unit. The second was the activated carbon unit which was sampled for comparative purposes. The third sample point was the effluent of the ORG. The fourth sample point was the effluent of the OPP. Data were collected for approximately 120 d. The entire data set for flow rate and temperature are presented in the following section for discussion purposes. Specific data sets at 0.6 m^3/d for toxicants reflect only 28 d of continuous flow.

RESULTS AND DISCUSSION

Biotreatment of dilute organochlorine-contaminated ground water

Two dilute ground water streams were treated during the course of the field pilot study (see Figure 3). Toxaphene (TOX), the primary waste constituent of concern in this

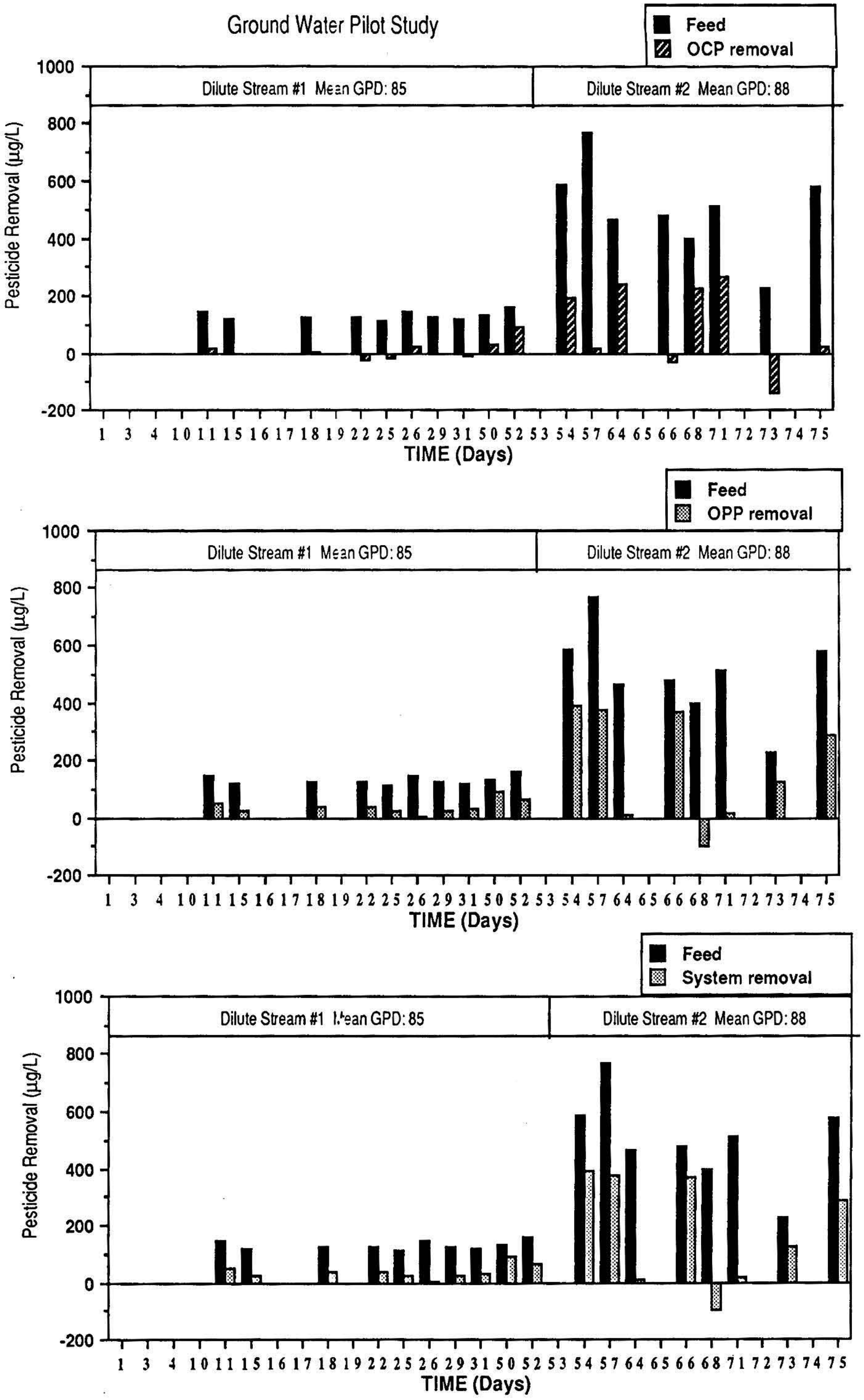

Figure 3. Pesticide removal rates for both organochlorine (OCP) and system immobilized bioreactors.

process stream, was evaluated for microbial mineralization at a dilute and elevated levels of contamination. Feed concentrations entering the system varied between 50 and 150 μg/L for Dilute Stream #1. For this primary organochlorine waste constituent, total carbon loading rates were considered to be oligotrophic.

Part per billion (ppb) concentrations are rather difficult to achieve notable process performances due to the low threshold values of substrate availability. This was particularly apparent for toxaphene. As shown in Figure 3, the first bioreactor, designated OCP, demonstrated minimal rates of removal at such dilute concentrations. Negative removal rates for days 22, 25, and 31 represent pulses of elevated TOX entering the system due to fluctuations in the well pump and feed tank. A mean removal rate of 44 μg/L was seen for the first reactor.

The second reactor, containing a small bed volume of organochlorine-degrading microorganisms, as well as a top layer of carrier containing organophosphate-degrading microorganisms, provided an elevated biotransformation rate. As shown in Figure 3, significant improvement for treatment of TOX was seen. A mean removal rate of 112 μg/L was realized for the OPP reactor. This is also reflected in the system removal rates, shown in Figure 3,

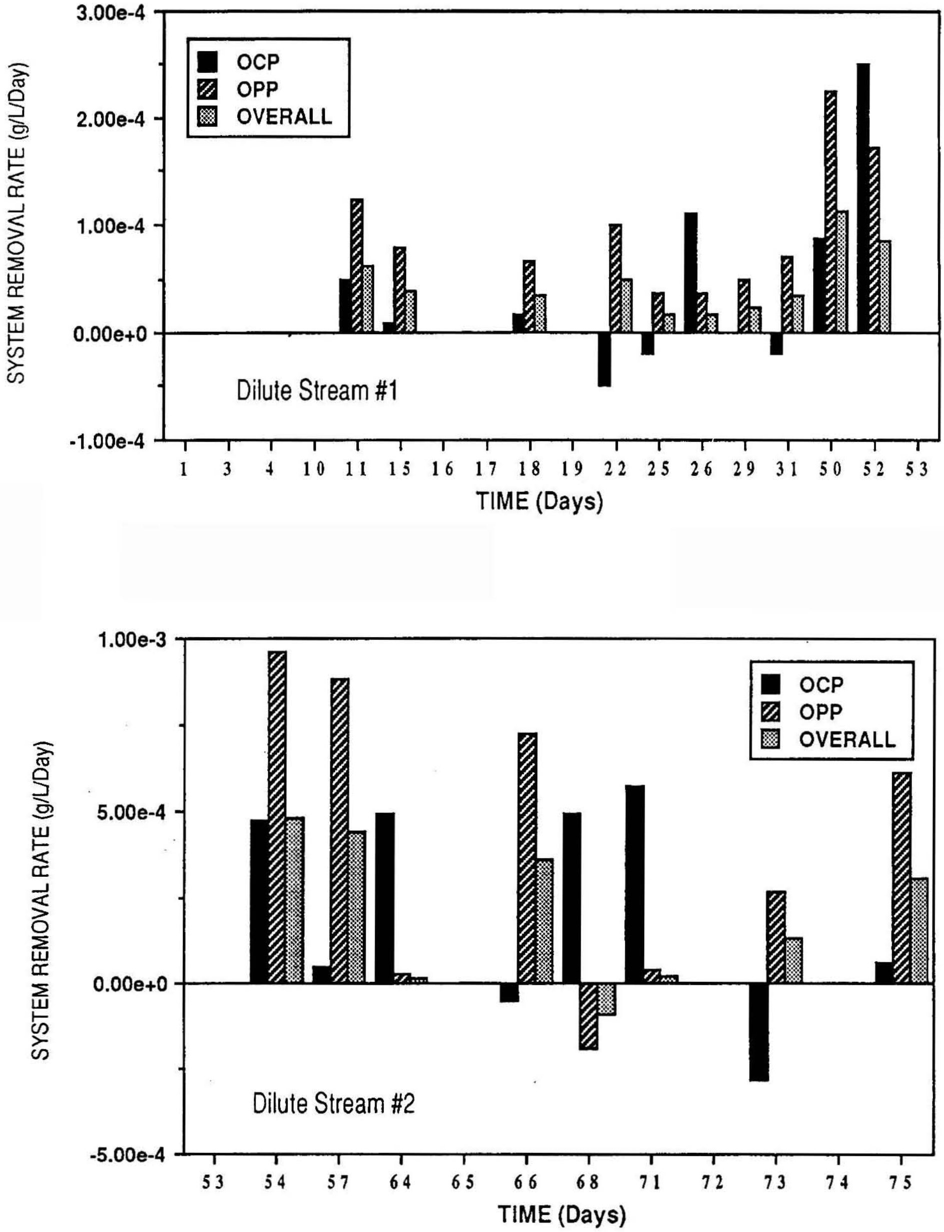

Figure 4. Kinetic rates of toxicant biotreatment for contaminated ground waters at two dilute concentrations.

wherein the combined bed volumes of both reactors are determined.

With increased total concentrations of toxaphene above the 200 μg/L concentration, Dilute Stream #2, improvements in process efficiency at 88 gpd (mean) were noted (see Figure 3). To summarize, the average reduction of toxaphene was 65% for the OCP and 54% for the OPP. Negative rate removal values reflected the transport of significantly high concentrations of TOX through the system as a result of settling phenomena in the phase separator. These intermittent pulses of TOX and surfactant associated with the ground water exceeded 1500 μg/L. Subsequent field tests employed the use of a mixer to ensure homogeneity of concentrations in ground water TOX concentrations.

System Removal Rates

Figure 4 presents data on removal rates of this dual column immobilized bioreactor system for TOX. Again, variations in homogeneous TOX feed are shown as negative rates of removal. The elevated TOX stream, designated as Dilute Stream #2, demonstrated almost an order of magnitude improvement in biotreatment efficiency, based on a g bed carrier dry weight/L ground water/day continuous treatment. The extremely oligotrophic stream, designated as Dilute Stream #1, showed improvements in TOX rates of removal only for days 50–53 when elevated TOX concentrations were recovered from the phase separator.

Organophosphate Removal

Although not presented graphically, organophosphate removals for both dilute ground water streams did not exceed 35% removal. The primary organophosphates were dioxathion and methyl parathion. It is believed that the reason for minimal organophosphate removal can be attributed to the following: the lack of separation of microbial populations between reactors, i.e., a biological solids removal system, may have resulted in exogenous biomass from the organochlorine population providing an available substrate for the organophosphate population. Thus, the presence of organophosphates in the ground water served as a phosphate source rather than a carbon source.

Carbon Usage

An activated carbon unit(s) was placed after biological solids removal to polish residual TOX, organochlorine and organophosphates residuals from each respective treatment stream. The carbon volume was 0.2 m^3. Earlier isotherm studies on this ground water indicated a carbon requirement of 2.5–10.0 g/L needed to meet regulatory discharge approval. For the entire Phase II study wherein a biological system was functioning as a pretreatment unit to activated carbon, the carbon requirement was estimated to be 0.10–0.25 g carbon/L of ground water (based on 45 d, 0.6 m^3/d, 167.4 μg/L TOX).

CONCLUSION

The diatomaceous earth surfaces used in this study appeared to be most effective in maintaining a stable microbial population throughout the course of this study. These surfaces demonstrated insulation of the microbial population to significant perturbations toxicant concentration. These immobilized bioreactors functioned as a conventional plug flow reactor. Thus, hydraulic retention times were notably short, i.e., 11 h for TOX.

The *Acinetobacter* species used appeared to be most effective in handling a rather complicated organochlorine at a dilute concentration. Furthermore, it is apparent that these adapted microorganisms selectively utilized the organophosphate constituents of the ground water waste stream when appropriate nitrogen/phosphorus demands were needed to achieve complete mineralization.

An evaluation of the effectiveness of pretreating biologically the ground water stream prior to activated carbon indicates a significant savings, based on dosing rate. Thus, it can be proposed that biological pretreatment of targeted ground water streams can be considered an appropriate adjunct to conventional carbon adsorption technologies, where significant reductions in carbon requirements can be realized. This, of course, translates into notable improvements in the economics of using carbon to treat recognized ground water streams having significant recalcitrant compounds present.

Diatomaceous earth materials have been evaluated for immobilization integrity and performance for several targeted ground water toxicants. The performance of these materials under continuous flow conditions indicated acceptable biomass colonization and maintenance over time. Chlorinated materials, having minimal affinity to the inert matrix, were biotransformed to an acceptable degree using an upflow, packed-bed configuration.

ACKNOWLEDGMENTS

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Field Evaluation of Nitric Oxide Abatement with Ferrous Chelates

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The absorption of nitric oxide from flue gas streams presents some unique problems due to its low solubility in conventional scrubbing solutions. A process is being developed that utilizes an electrolytic cell to reduce Fe(III) to Fe(II) and maintain the majority of the iron chelate in the active ferrous state. This process has been tested on an actual flue gas stream and achieved 80% nitric oxide abatement. Further reduction of nitric oxide is possible with increased stages.

INTRODUCTION

The combustion of fossil fuels containing sulfur and nitrogen compounds produces oxides of sulfur and nitrogen. Most of the nitrogen oxide is formed in the high-temperature combustion from atmospheric nitrogen rather than from fuel-bound nitrogen. Ninety to ninety-five percent of the nitrogen oxide in combustion flue gas is nitric oxide (NO), with the balance being mostly nitrogen dioxide. The absorption of nitric oxide from flue gases presents some problems because of its low solubility in conventional scrubbing solutions. Ferrous chelates are known to enhance the absorption of nitric oxide. However, oxygen present in all flue gas streams oxidizes most of the active Fe(II) to the inactive Fe(III). This results in high iron chelate concentration requirements and leads to prohibitive iron chelate loss rates.

A process is being developed that utilizes an electrolytic cell to reduce Fe(III) to Fe(II) and maintains the majority of the iron chelate in the active ferrous state. This process has been tested on an actual flue gas stream and achieved 80% nitric oxide abatement. Further reduction of nitric oxide is possible with increased absorber stages. The electrochemical cell successfully reduced Fe(III) to Fe(II) and maintained greater than 90% of the total iron as Fe(II). This paper summarizes the field test results.

THEORETICAL BACKGROUND

Fuel combustion processes produce oxides of sulfur and nitrogen, primarily sulfur dioxide and nitric oxide. Sulfur dioxide can be scrubbed from flue gases by contacting the gas with an alkaline absorbent such as caustic, lime, or limestone. Nitric oxide is difficult to absorb in aqueous scrubbing solutions due to its low solubility. Ferrous chelates are known to enhance the absorption of NO by reacting to form a ferrous nitrosyl complex.

What are Chelates?

A chelate is a metal-chelant complex. A chelant or chelating agent is a ligand that contains more than one electron donor group and can form a complex with a metal ion. Ligands generally contain a functional group with a negative charge or a lone pair of electrons. Some examples of chelating agents are nitrilotriacetic acid (NTA),

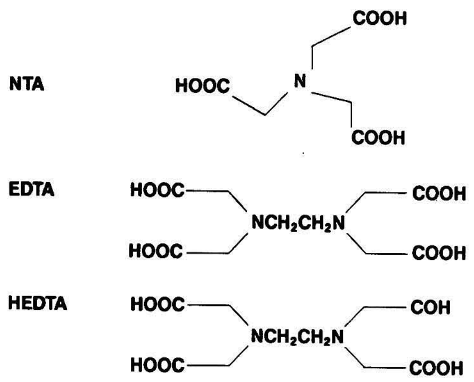

Figure 1. Common chelating agents.

ethylenediaminetetraacetic acid (EDTA), and hydroxyethylethylenediaminetriacetic acid (HEDTA), represented in Figure 1. Chelants tie up metal ions in solution so that higher metal and hydroxide concentrations are permitted without metal hydroxide precipitation.

Ferrous chelates increase the absorption rate of NO by reacting stoichiometrically with NO to form the ferrous nitrosyl complex, as shown in equation (1). This greatly increases the solution's NO capacity.

$$\mathrm{Fe(II)\,L + NO \leftrightarrow Fe(II)\,(L)\,NO} \tag{1}$$

Once in solution, NO reacts with sulfites produced by SO_2 absorption to form various nitrogen/sulfur compounds and regenerates the chelate, as shown in equation (2).

$$\mathrm{Fe(II)\,(L)\,NO + SO_3^{=} \rightarrow Fe(II)\,(L) + S,\,N\ products} \tag{2}$$

The reduction seems to be rather complicated, and different reduction products have been reported under similar reaction conditions. Chang and Littlejohn [*1*] have determined several species of mixed sulfur-nitrogen salts along with molecular nitrogen and nitrous oxide. The distribution of these products is very dependent on reaction conditions.

The effectiveness of ferrous chelates to abate NO is well documented [*2*]. The major problem hampering the commercial development of this process is that the oxygen present in the flue gas oxidizes most of the ferrous chelate to the ferric chelate, as shown in equation 3, which has little affinity for nitric oxide.

$$\mathrm{4\,Fe(II)\,L + 4\,H^+ + O_2 \rightarrow 4\,Fe(III)\,L + 2\,H_2O} \tag{3}$$

Oxidation of Fe(II) by NO can also occur [*3*]. Though reduction of trivalent iron by sulfites, as shown in equation (4), competes with the divalent iron oxidation, as shown in equation (3), the majority of the iron will remain in the inactive trivalent state.

$$\mathrm{Fe(III)\,(L) + SO_3^{=} \rightarrow Fe(II)\,(L) + \frac{1}{2}\,S_2O_6^{=}} \tag{4}$$

Therefore, a high concentration of iron chelate is required and blowdown to purge sulfur/nitrogen salts results in iron chelate losses that render the process uneconomical.

Development is continuing on this patented process, which utilizes an electrochemical cell (see Figure 2) consisting of cathode and anode compartments separated by membranes for ferric chelate reduction [*4*]. The scrubbing solution containing ferrous and ferric chelates is circulated through the cathode compartment and an electrolyte is circulated through the anode compartment. As current is applied to the electrochemical cell, ferric chelate is reduced in the cathode compartment to ferrous chelate and water is electrolyzed at the anode to oxygen and hydrogen ion. The electrochemical cell maintains the majority of the iron chelate in the active ferrous state, which decreases the total iron chelate requirement and decreases the iron chelate loss rate. A simplified schematic of this process is shown in Figure 3.

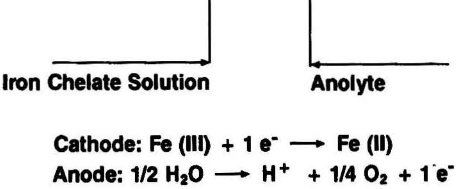

Figure 2. Electrolytic cell.

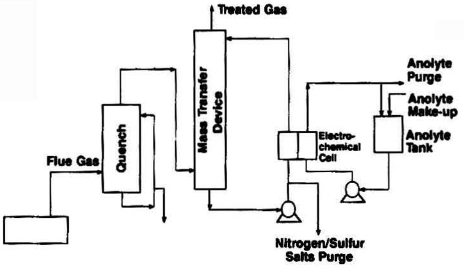

Figure 3. Simplified schematic of NO_x abatement process.

FIELD TESTING

To determine the performance capability of this process, a field test was conducted on an actual flue gas stream.

Equipment Description

The field trial was conducted on a sidestream of an actual flue gas stream. A schematic of the field trial apparatus is shown in Figure 4. The exhaust gas, typically 28.3 m^3/min (1000 ACFM), flowed through a 0.2 m (8 in) diameter light-gauge, steel duct to the first absorber where it flowed upwards countercurrent to the iron chelate scrubbing solution. After it left the first absorber, it was ducted to the second absorber where it again flowed upwards countercurrent to the iron chelate scrubbing solution. The absorbers were each 0.61 m (2 ft) in diameter, packed with 1.22 m (4 ft) of Norton size 1 plastic SUPER INTALOX packing.

The scrubbing solution holding tank, D-4, was a 1.067 m (3.5 ft) diameter FRP (fiberglass reinforced plastic) tank. The scrubbing solution was pumped from this tank by a centrifugal pump to a header system that distributed the scrubbing solution to the absorbers. The header system consisted of rotameters and valves which

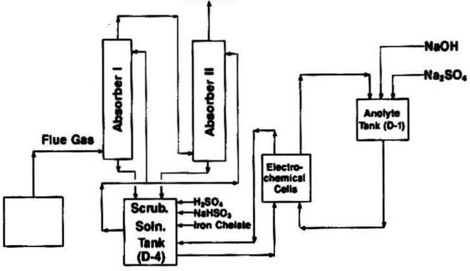

Figure 4. Schematic of field trial apparatus.

controlled the liquid flow to each absorber at 4.54 to 5.68 m^3/hr (20 to 25 GPM). A sidestream was circulated through a pH probe and the scrubbing solution pH was typically maintained by addition of acid. The solution leaving the absorbers was returned to the top of the FRP holding tank. The scrubbing solution was pumped by a centrifugal pump to the bottom of the cathode compartments of the electrolytic cells where the Fe(III) was reduced. The flow rate of this solution was measured by a vortex flowmeter and controlled by a flow controller. The catholyte solution exited from the top of the cells and was combined for return to the FRP tank (D-4).

The anolyte solution holding tank (D-1) was also an FRP tank. The anolyte solution was pumped to the anode compartments of the electrolytic cell by a centrifugal pump. The anolyte solution flow rate was measured by a vortex flowmeter and controlled by a Taylor flow controller. The anolyte solution exited from the top of the cells and was combined for return to the anolyte holding tank (D-1). A pH electrode monitored the pH of the anolyte at the pump recycle. This pH was controlled by a Taylor Microscan controller that pneumatically adjusted the speed of the NaOH metering pump. A 10% Na_2SO_4 solution was metered into the anolyte solution tank to replace sodium sulfate lost in the anolyte purge. The NaOH and Na_2SO_4 metering pump was a Milton Roy "A" duplex disc diaphragm controlled volume pump. The NaOH pump was pneumatically actuated by a pH controller. DC current is supplied to the two electrolytic cells by two air-cooled rectifiers.

Experimental Procedure

The initial scrubbing solution was a 0.719 m^3 (190 gallon) mixture of 0.012 M iron chelate and 0.5 M $NaHSO_3$. The anolyte solution was 0.795 m^3 (210 gallons) of 0.5 M Na_2SO_4. These concentrations were determined by the amount of nitric oxide removal desired. Sodium hydroxide was gradually added to bring the scrubbing solution pH to 6.0 and the scrubbing solution circulated through the electrolytic cells to reduce the ferric chelate. When the majority of the ferric chelate had been reduced, flue gas and liquid circulation were started through the absorbers. The pH of the scrubbing solution was controlled at 6.5. The pH of the anolyte was controlled at 7.0.

Sulfites are required in this process. In flue gas streams, which contain SO_2, sulfite requirements are provided by the absorbed SO_2. This flue gas did not contain any SO_2, therefore, sodium bisulfite was continuously added to the scrubbing solution. Typically, the unit ran attended 24 hours per day. Operating data and liquid and gas analyses were obtained throughout the day. Table 1 shows typical conditions.

TABLE 1. TYPICAL FIELD TEST CONDITIONS.

Flue Gas Flow Rate	28.3 m^3/min (1000 ACFM)
Flue Gas Conditions	
NO Concentration	40 PPM
Oxygen Concentration	14.5%
Carbon Dioxide Conc.	3.5%
Sulfur Dioxide Conc.	0%
Temperature	350 K (170°F)
Scrubbing Solution	
Scrubbing Solution Flowrate	4.54 m^3/hr/Absorber (20 GPM)
Fe(II) Concentration	0.01 gmoles/liter
Fe(III) Concentration	0.0004 gmoles/liter
pH	6.5
Sulfite Concentration	0.1–0.2 gmoles/L.
Temperature	322 K (120°F)

RESULTS AND DISCUSSION

Nitric Oxide Abatement

The overall nitric oxide abatement achieved ranged from 70% to 80%, with each absorber removing approximately 50% of its feed nitric oxide concentration. The NO concentration was typically reduced from 40 ppm to 20 ppm in the first absorber and then was further reduced from 20 ppm to 10 ppm in the second absorber. Nitric oxide feed concentration had very little effect on the percentage of nitric oxide abated. Nitric oxide feed concentration was spiked to 150 ppm and 700 ppm for several hours each. The overall absorption remained at 70% to 80%.

This is in agreement with the HTU (height of a transfer unit) concept, the idea of which is to divide the packed section into a number of contact units. One transfer unit is the height of packing one unit. For a given separation in a system where the mole fraction of absorbed species at the gas-liquid interface is essentially zero [5], the number of gas phase transfer units is calculated by:

$$N_G = \mathrm{Ln}\,(Y_1/Y_2) \qquad (5)$$

where,

Y_1 = mole fraction NO in the feed gas

Y_2 = mole fraction NO in the outlet gas

Equal heights of packing therefore achieves equal percentage reduction of nitric oxide, regardless of nitric oxide concentration. This is in agreement with the observation that each absorber with four feet of packing achieved 50% nitric oxide abatement, although the feed NO concentration varied. The height of a transfer unit is a function of mass velocities of gas and liquid, the viscosity, density and diffusivity of the fluids, and the size and shape of the packing [6].

The literature also supports this result. Tanaka et al. [7] reported that if a tower with a given height of packing achieved 80% denitrification, doubling the packing height would increase the denitrification rate to 96%. If one examines this in terms of the HTU concept, one finds that 80% denitrification corresponds to 1.61 transfer units and 96% denitrification corresponds to 3.21 transfer units, or exactly twice the transfer units.

Effect of Fe(II) Concentration

A set of laboratory runs was made prior to the field trial to obtain some preliminary data. The lab scrubber was

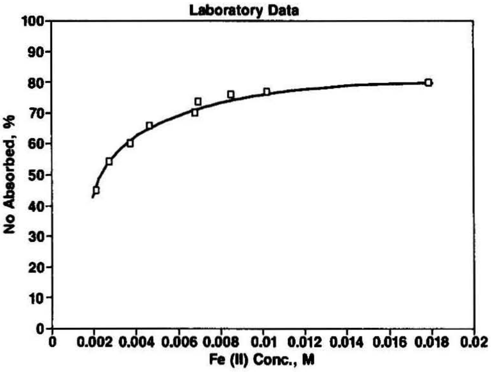

Figure 5. NO absorption vs. Fe(II) conc.

0.051 m (2 in) I.D. glass column with 0.381 m (15 in) of ceramic Intalox saddles. The feed gas was 0.368 m^3/hr (13 SCFH) of simulated flue gas containing 15% O_2 and 150 ppm NO. The percentage of nitric oxide abatement versus Fe(II) concentration is shown on Figure 5. The nitric oxide abatement is a function of Fe(II) concentration only when the Fe(II) concentration is less than about 0.009 M. Nitric oxide abatement increased from 45% to 76% when Fe(II) concentration increased from 0.002 M to 0.009 M. Increasing the Fe(II) concentration from 0.009 M to 0.018 M only increased NO abatement from 76% to 80%. This finding was duplicated during the field trial. The nitric oxide abatement remained between 70% and 80% as the Fe(II) concentration was increased from 0.009 M to 0.03 M in this set of absorbers. Additional mass transfer stages would have resulted in increased abatement.

Reaction Products

Ion chromatographic analyses of several samples completed after the field trial showed that sulfite, sulfate, thiosulfate, and hydroxylamine disulfonate were the major components of the scrubber effluent. Hydroxylamine monosulfonate and amine disulfonate were not detected in the samples. Ion chromatography showed no signs of nitrite. Analysis of vent gas samples showed no detectable N_2O.

Electrochemical Cell Operation

The electrochemical cell operated very smoothly to maintain the majority of the iron chelate in the active ferrous chelate form. The current required by the electrochemical cell is determined by the amount of oxidation that occurs in the absorber. The rate of oxidation is determined by many factors, including the volume of the flue gas treated, absorber design, oxygen concentration, and temperatures. Examination of the electrodes and membranes at the conclusion of the field trial showed no significant changes. However, no predictions about their ultimate lifetimes can be made without further testing.

SUMMARY

Ferrous chelate-based processes are promising because of their ability to absorb sulfur oxide and nitrogen oxides in a single process and their suitability for integration into existing wet flue gas desulfurization processes. The field test demonstrated that iron chelates in conjunction with electrolytic ferric chelate reduction are very effective for nitric oxide abatement. The electrochemical cell effectively reduces ferric chelate to ferrous chelate and maintains the majority of the iron chelate in the active ferrous state. The chemical and electrical requirements for the process depend on such flue gas conditions as oxygen content, NO content, SO_2 content, and the level of NO removal required. A suitable commercial site is being sought for further testing.

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Improved Clarifier Performance and Capacity Through the Use of A Flow Contraction Baffle

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Pilot-scale tests were conducted over several years on the effectiveness of a flow contraction baffle installed in a pilot-scale clarifier to separate solids from both primary sewage and activated sludge mixed liquor. Tests used two matched, 1.2-m diameter clarifiers, one of which was fitted with the baffle, in the form of a truncated cone descending from the effluent weir. Effectiveness of the flow contraction baffle results from the suppression of additive interference of density waves always present in clarifiers as well as provision for the uniform withdrawal of the clarified liquor.

INTRODUCTION

The faith environmental engineers place in the rates of separation predicted by quiescent settling measurements made in standard sedimentation cylinders indicates the widespread, though erroneous belief that clarification represents the superposition of quiescent disengagement of solids from their suspension in a flowing liquid. The presence of a density gradient in a moving fluid, a necessary condition for settling, changes the hydrodynamics of flow significantly. Stratified flow occurs under settling conditions; the properties of this type of flow can be utilized to improve clarifier performance. Testing of a device for this purpose is the subject of this paper.

STRATIFIED FLOW AND FLOW CONTRACTION

The presence of suspended solids in moving liquids leads to unique patterns of flow behavior. These have been known for over a hundred years, but have not been applied to clarification. In addition to the possibility of internal waves, distortion of the flow lines in front of bluff objects and the phenomenon of selective withdrawal may be observed.

Internal waves result from the presence of a vertical density gradient in a clarifier. A vertical density gradient is inevitable if settling occurs. The initiation of waves is explained in Figure 1. Disturbances displacing slurry elements within the density gradient induce internal waves [*1*, *2*]. The low viscosity of the aqueous medium provides only small damping to this motion; thus, the motion continues as a slowly damped oscillation. Reflections from clarifier walls set up interference patterns and large-amplitude waves appear in a chaotic fashion. These waves retard settling of the solids probably in proportion to the amplitude of the disturbances.

Figure 2 shows a trace of the density variations referred to as waves inside a clarifier. The trace was made by placing small fiber optics light probe/turbidimeter inside a model rectangular clarifier [*3*, *4*]. It has been known for many years that internal waves, like surface waves, propagate at relatively low speeds, reflect around a vertical axis, and damp out very slowly. Internal waves reflecting off clarifier walls interfere with waves moving toward the wall resulting in large-amplitude waves (the large, relatively infrequent disturbances in Figure 2).

Because the most minute disturbance can cause internal wave formation, preventing wave generation appears to be an impossible task. Our research has, therefore, concentrated on flushing internal waves out of the clarifier, thereby reducing interference and the build-up of large waves. This has been done by creating a wave trap near the outlet weir by means of flow contraction geometry (called a flow contraction baffle). A flow contraction baffle design has been patented [*5*, *6*]. We refer to it as the Waterloo Clarifier. Two versions of this clarifier design are shown as Figure 3. Flow contraction has the additional advantage that it promotes uniform withdrawal of the clarified liquor. In stratified flow, line or slit withdrawal caused by an outlet weir leads to withdrawal from mainly the uppermost fluid layer. This sets up shear forces which cause slow mixing of the clarifier content.

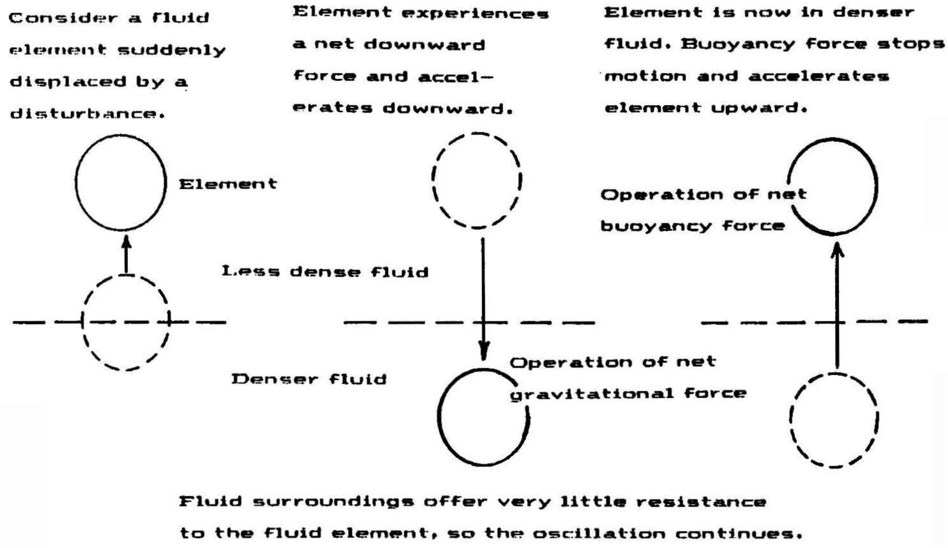


Figure 1. Mechanism of internal wave formation.

A much more complete examination of stratified flow and its consequence for clarifier operation is given by Cordoba-Molina, et al. [3]; further papers discuss the physics of the flow contraction baffle [*4*, *7*]. The effect of flow contraction on internal waves is described by Murphy, et al. [8].

Objectives

The work reported in this paper was undertaken to determine the performance of flow contraction baffles when used on the clarification of real waste streams. It is the logical extension of laboratory work to test the principle. This work has been discussed by Cordoba-Molina, *et al.* [7], Silveston, *et al.* [8], and Wigglesworth, *et al.* [9].

EQUIPMENT AND PROCEDURES

Flow Contraction Baffle

Flow contraction is achieved by flowing the contents of the settling tank radially from the center across the upward-slanting inner surface of a truncated cone. This conic section of galvanized sheeting is referred to as the "flow contraction baffle." Figures 3a and 3b are scale drawings of this construction, omitting the rakes used to scrape off the settled sludge. In Figure 3a, the baffle extends to the clarifier floor. Laboratory work shown in Figure 4 demonstrates that a full baffle is not necessary [9]; a partial baffle can be used. In Figure 3b, a partial baffle is shown reaching only halfway to the clarifier floor. Because a full flow contraction baffle would interfere with the rake arms, only the partial flow contraction baffle is of interest from the point of view of retrofitting an existing clarifier to improve its performance; just the partial flow contraction baffle was tested in this study. All measurements were made on 1.2 m (4 ft) diameter clarifiers. Essential dimensions are given in the figures. The clarifier equipped with a baffle was paired with a second clarifier identical in every way except for the baffle, for most of the pilot runs.

Tanks and the flow contraction baffles were constructed of carbon steel; the latter were attached to the tank side-

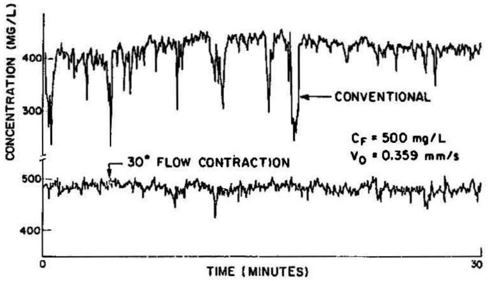


Figure 2. Instantaneous density variations within clarifiers with and without a flow contraction baffle.

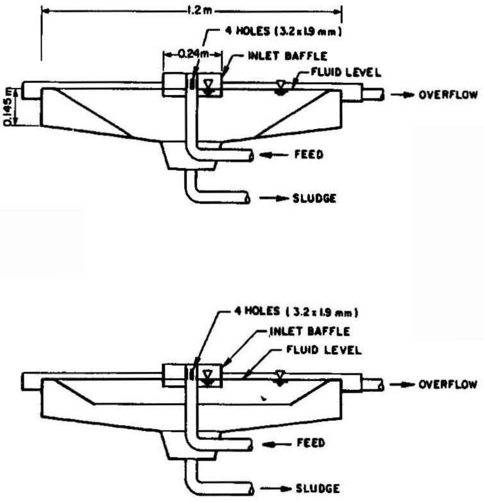
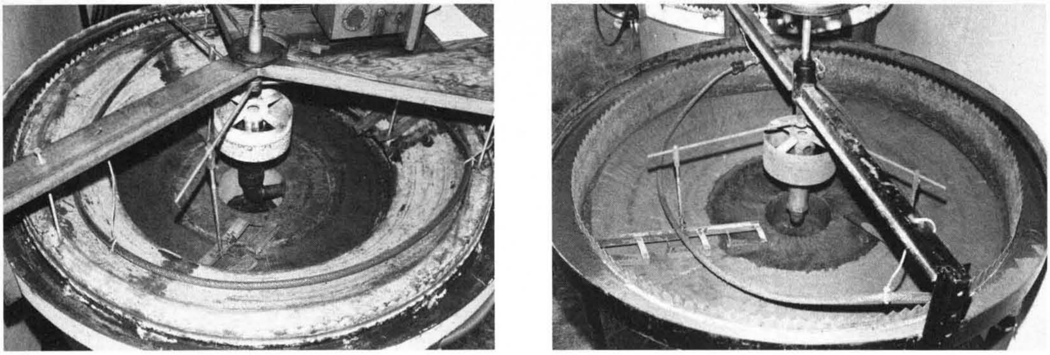


Figure 3. Schematics of a) full and b) partial flow contraction baffles built into the 1.2-m diameter pilot-scale clarifiers.



(a) (b)

Figure 4. Photographs of the pilot clarifiers showing center well, weir, scrapers and the floating hose section used for scum selection. a) Clarifier equipped with flow contraction baffle, b) Unbaffled clarifier.

wall. Tank bottom and the baffle were scraped by separate arms mounted on the same shaft moving at about 3–4 revolutions per hour. Scrapers and their location can be seen in Figure 4a. Scrapers and arrangement for the unbaffled tank used in most of the tests are shown in Figure 4b. The scrapers were driven by the motor on the baffled tank; pulleys were sized so that the scraper revolutions per hour were identical. As may be seen in the photographs, center feed was used with identical baffles to reduce inlet disturbance and distribute the feed. The saw-tooth peripheral overflow weir can also be seen. A satisfactory scum trap was provided by the rubber hose that floated on the surface when the clarifiers were in operation.

Test System

The majority of the experiments reported were carried out in the Little River Pollution Control Plant operated by the Public Works Department of the City of Windsor. This plant, which is rated at 8 million Imperial gallons/day, is located in the eastern outskirts of the city and handles a predominantly domestic waste. There is an industrial and commercial component; the former arises largely from the metalworking industry. During late summer, the Little River Plant receives canning wastes. These introduce large day-to-day variations in BOD and suspended solids. A screened raw sewage was used for one set of tests, while a second and third set employed the mixed liquor feed to the secondary clarifier. The latter set was carried out in the summer of 1986, while the former two sets were performed from May to December in 1984.

A siphon was used to withdraw the screened raw sewage from a header feeding the plants' two primary clarifiers and also to withdraw mixed liquor from the channel connecting the aerators to the secondary clarifiers. Underflow was by gravity for the first and second test sets on the raw sewage and aerator mixed liquor, respectively. The underflow was set at about 50% by volume, but was not closely controlled. For the third set of tests, the high overflow rates required pumping of the aerator mixed liquor to the model clarifiers and withdrawal of the underflow under suction. Underflow was held closely to 50% of the liquor feed by volume.

In the first set of tests, a single clarifier was used and flow contraction baffles were used for a one week run, then removed for a run performed during the following week. These alternating baffle/no baffle runs indicate a 10% to 13% increase in removal efficiency (weight of suspended solids removed during test/weight of solids fed to the clarifier during the same period). The alternating baffle/no baffle was the procedure used in an earlier pilot-scale study of a secondary clarifier carried out in Pilot Plant #1 at the Wastewater Technology Centre, Canada Centre for Inland Waters (Burlington, Ontario). Results from this study, a reduction in effluent suspended solids between 32% and 50%, are discussed by Hudgins and Silveston [*10, 11*].

Interpretation of the results for the single clarifier was different because of the wide variation in the solids loading and settleability of the raw sewage caused by canning wastes flowing to the plant and the intermittent use of aluminum chloride for phosphorus removal, so a second pilot scale clarifier, identical in internal dimensions to the original unit, was constructed. These two clarifiers operating in parallel were used for the remainder of the first set of tests, as well as for the tests on secondary clarification.

To accommodate two parallel units, the siphon line was rebuilt with two branches, but switchable so that either could feed each of the pilot clarifiers. This arrangement was used for the first and second test sets. For the third set, separate pipes outfitted with Moyno SP (Model 35601) positive displacement pumps were used to withdraw flow from the channel to feed the paired clarifiers. These pipes were fitted with switching valves to divert the flows to either one of the clarifiers. Flows were redirected periodically so that the flow withdrawal produced no bias in the tests.

At the high hydraulic loadings used, the head in the clarifier was inadequate to give the underflow rates needed for a 50% flow split. Moyno SP (Model 34401) positive displacement pumps were used to suck underflow from the clarifiers. The test installation, including all the pumps, and the paired clarifiers, were housed under a protective shed.

Data Collection

Performance data were collected from grab samples taken at the clarifier inlet and in the overflow at hourly intervals. Inlet and outlet sampling times allowed for the residence time in the clarifier and feed lines. Suspended solids in these samples were measured by filtration and weighing following standard procedures [*12*]. Duplicate measurements were always made. Overflow and underflow rates were checked regularly. These were found to

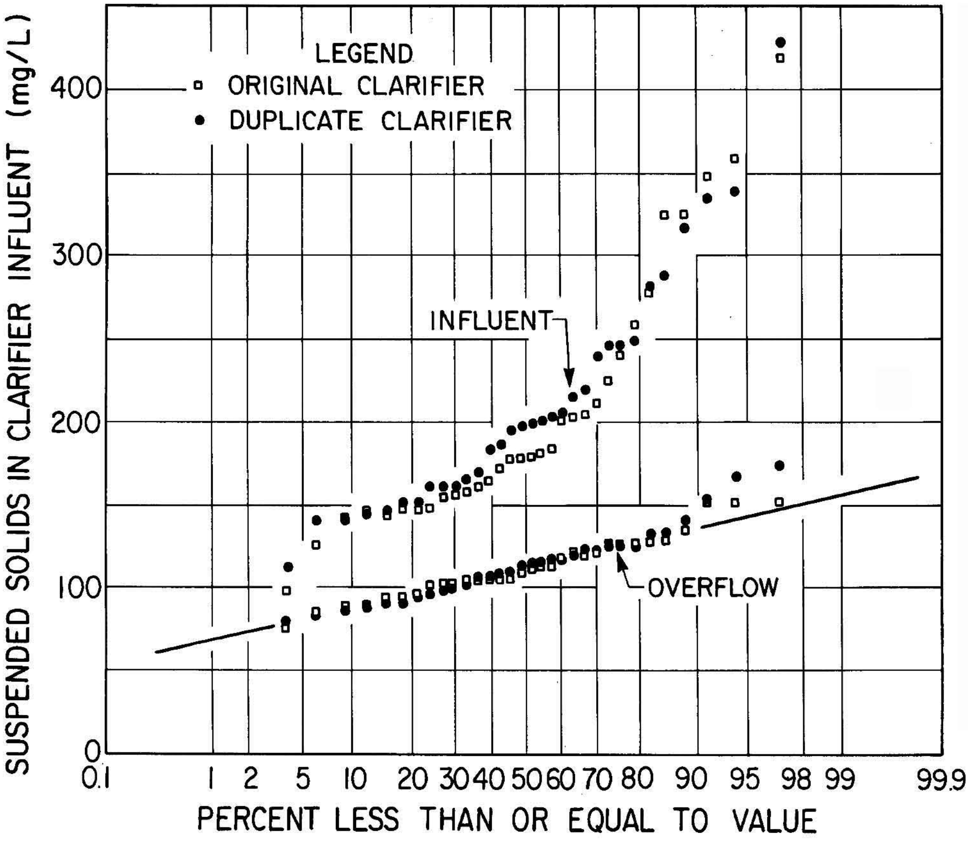


Figure 5. Comparison of the performance unbaffled, geometrically identical pilot scale clarifiers on screened raw sewage (overflow rate = 40 m^3/m^2 · d).

be constant throughout the test duration regardless of whether pumps were used to provide underflow suction.

In the third set of tests, quiescent settling tests were performed daily and the sludge volume index was measured every several days. Again, standard procedures were employed. Settling tests were performed less frequently in the first and second test sets.

Standardization Tests

Tests were undertaken to demonstrate that the paired clarifiers performed identically when both were unbaffled. The tests also served to show that there was no bias introduced by the feed system. Standardization tests were carried out at 40 and 20 m^3/m^2 · d in the first and second tests, respectively, while in the third set, they were performed at 22, 28, and 64 m^3/m^2 · d. Experiments at each overflow rate were performed over at least five days and the feed arrangements were switched once.

Typical data are plotted in Figure 5 for an overflow rate of 40 m^3/m^2 · d. The figure shows the influent raw sewage suspended solids concentration and the overflow suspended solids on probability paper. No significant difference was found between the means of the twinned unbaffled clarifiers. Results for the mixed liquor feed with overflow rates ranging from 20 to 47 m^3/m^2 · d were the same: there was no significant difference between the means of the two pilot-scale clarifiers. At the 64 m^3/m^2 · d overflow rate, only about a 50% reduction of the suspended solids was achieved. This occurred because the sludge level reached the upper surface of the clarifier, causing excessive carryover of solids into the effluent weir. Even under these conditions, there was only a 5% difference in clarifier performance, which was not significant statistically. It is clear that the clarifiers perform identically and, furthermore, there is no significant bias in the feed arrangements. Nevertheless, feed arrangements were switched at least once in all the remaining tests.

PRIMARY CLARIFICATION

Measurements were made on the paired, parallel operating clarifiers over two consecutive four-day (weekday) periods at a constant overflow rate to each pilot clarifier equal to 40 m^3/m^2 · d (800 Imp · gal/day-ft^2). Sixty-nine measurements were made on both the feed and the overflow of each clarifier. Results were plotted on probability paper and shown as Figure 6. Percent removal of suspended solids has been used because this is the important performance variable for primary clarification.

The overflow rate used in this test represents a daily mean overflow rate that is often found in municipal sewage treatment plants. It was also the rate used in the standardization test, which showed both clarifiers performed identically.

Figure 6 shows clearly that the flow contraction baffles improves the separation of solids achieved in primary clarification. At the median point of the 69-point data set,

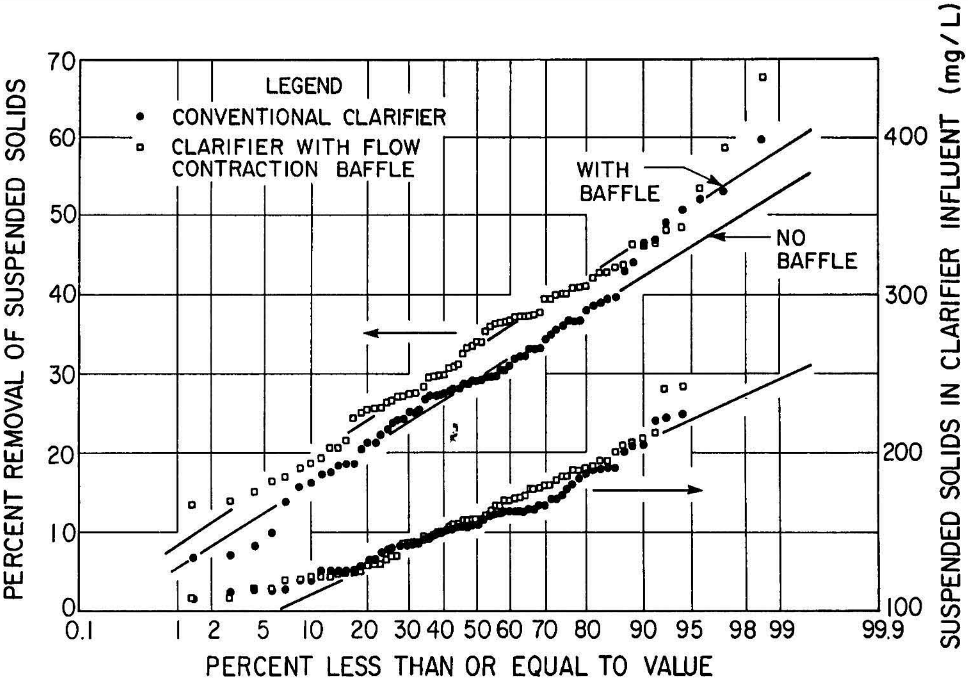


Figure 6. Comparison of the raw sewage performance of a pilot scale clarifier equipped with a flow contraction baffle with an identical but unbaffled clarifier. Overflow rate for each clarifier was held constant at 39 m³/m² · d. Underflow rates were also held identical.

the improvement ranges from 12% to 15%, but improvement is evident at all other decile points. Influent suspended solids to each of the clarifiers varied from one measurement to another as Figure 6 shows, but on probability paper, the influent suspended solids data sets for the paired clarifiers overlap completely and form a single population. Statistical analyses of the data (t-tests) confirm that the baffle improves performance. Even plots of daily means [*13*] show a distinct improvement resulting from the flow contraction device.

Primary clarification involves mainly non-flocculating, essentially ideal settling solids. Because such settling systems were exhaustively studied in our laboratory [*4, 5, 8, 9*] further pilot plant measurements at lower overflow rates were not pursued. Measurements at higher overflow rates were not possible because of the total flow limitation of the siphon system.

SECONDARY CLARIFICATION

Zone settling and thickening are the dominant phenomena in the clarification of such biosolids as found in the mixed liquor obtained from aerators in the activated sludge system. Suspensions with this settling behavior were not tested in our laboratory. However, prior to the tests at the Little River Pollution Control facility, some experiments employing municipal wastewater were performed in Pilot Plant #1. Raw sewage from a nearby waste treatment plant was fed to the pilot plant through a hydrasieve. This plant did not contain a primary clarifier, so the influent entered the aerator directly. Clarification of the aerator mixed liquor was performed in a 2.4-m diameter circular clarifier; details are given by Hudgins and Silveston [*11*]. Measurements were made at overflow rates of 12.7 and 25.4 m³/m² · d for alternating periods of about two weeks during which the clarifier was operated with a flow contraction baffle and with the baffle removed. Suspended solids in the mixed liquor were within 2,000 mg/L ± 10%. Measurements were corrected to 2,000 mg/L using performance data for the unbaffled clarifier.

Figure 7 compares the mean overflow suspended solids

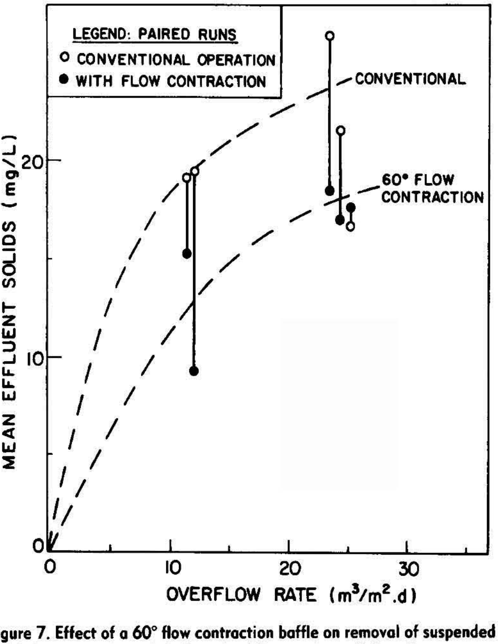


Figure 7. Effect of a 60° flow contraction baffle on removal of suspended solids from an activated sludge mixed liquor using a 2.4-m diameter secondary clarifier (corrected to 2000 mg/L mixed liquor concentration).

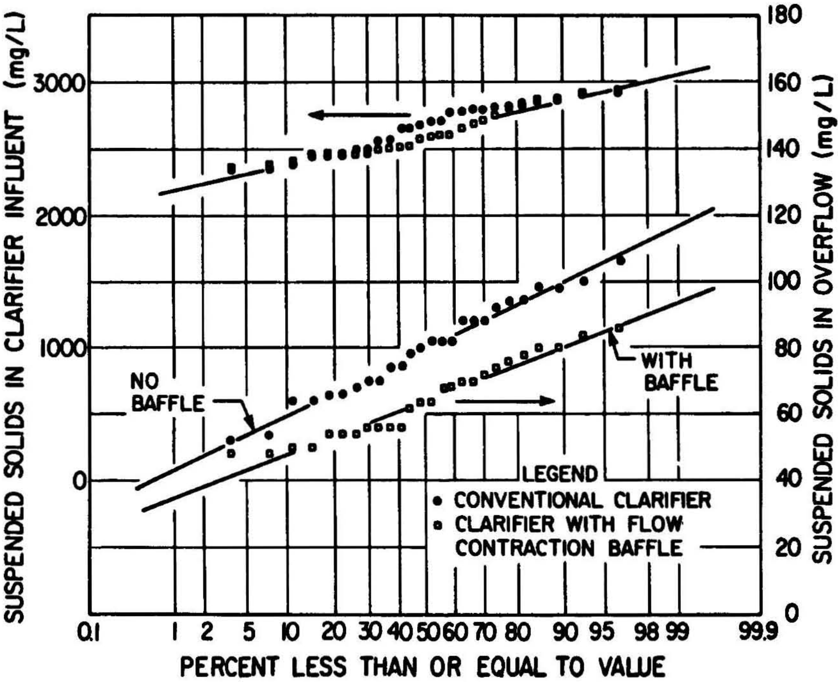


Figure 8. Effect of a flow contraction baffle on removal of suspended solids from aerator mixed liquor using paired circular clarifiers equipped with scum traps and operating at 20 m³/m² · d with 50% underflow.

for the 2.4 m diameter clarifier with and without the flow contraction baffle. The line connecting data points indicates measurements made in consecutive weeks. Neglecting the one data set out of five in which no improvement was found, curves through the weekly averages indicate about a 50% reduction in suspended solids in the overflow from use of a flow contraction baffle. Internal waves were evident in all clarifier tests from the continuous record of overflow turbidity. As expected, the flow contraction baffle caused a reduction in wave amplitude. This was indicated by changes in the suspended solids variability, measured as the standard deviation of the overflow suspended solids concentration. These data are contained in Figure 7, which show that an order of magnitude reduction in the standard deviation is found with flow contraction present.

Tests on the Little River Pollution Control Plant activated sludge mixed liquor were carried out in 1984 and 1986. In the former year, the paired clarifiers, operating in parallel, were fed by the siphon system used with raw sewage. Measurements were performed only at 20 $m^3/m^2 \cdot d$ and extended over twelve weekdays. Seventy-one measurements of both influent and overflow suspended solids were made respectively on each of the clarifiers. Additional runs were made with the paired, unbaffled clarifiers at 20 $m^3/m^2 \cdot d$ to demonstrate that they performed identically.

Data for the latter part of the data set (25 of 71 measurements) taken when both clarifiers were fitted with a scum collecting ring (see Figure 4) are given in Figure 8. It can be seen that flow contraction decreases solids loss to the overflow by about 20% at the median of the data. Roughly the same decrease was obtained when scum catches were not used on the clarifiers.

Data set 2 were repeated and the range of overflow rates extended in 1986 by adding feed pumps and pumping out the clarifier underflow. Tests were performed at overflow rates of 22 (6), 28 (8), 40 (5), 47 (5), and 64 (2) $m^3/m^2 \cdot d$. The numbers in parentheses indicate test length in days. In addition, standardization tests were performed at 22 (4), 28 (4), and 64 (5) $m^3/m^2 \cdot d$. Excessive solids in the overflow at 64 $m^3/m^2 \cdot d$ caused by sludge levels extending to virtually the free surface of the clarifier curtailed test data collection at 64 $m^3/m^2 \cdot d$. Severe scaling problems for clarifiers limit the overflow rates that can be tested with respect to the performance of the flow contraction baffles if real streams such as activated sludge mixed liquor, at concentrations encountered in practice are to be used. Maintaining geometric similitude in the clarifiers means that the depth at the clarifier centre is only 20 cm. Sludge compaction is limited so that as the loading increases, more sludge is held in the clarifier causing the level to rise. Geometric similitude was adhered to because fluid velocities scale with geometry and flow patterns (*e.g.*, by-passing, density currents) should also scale in this way. Sludge collection and handling do not scale with geometry. If the pilot-scale clarifiers were to model full-scale units using the same influent mixed liquor suspended solids concentrations, they would have to have the same depth as full-scale clarifiers (3 to 5 m). For example, a pilot clarifier 1.2 m in diameter and, say, 3 m in depth would grossly distort the flow patterns found in full-scale units.

Figures 9 and 10 plot the influent and overflow suspended solids on probability paper for the smallest and largest overflow rates (22 and 47 $m^3/m^2 \cdot d$) fully investigated. Table 1 gives a statistical evaluation of the vast number of measurements made. Both figures show that the influent mixed liquor suspended solids for the paired clarifiers overlaps; however, a very large difference can

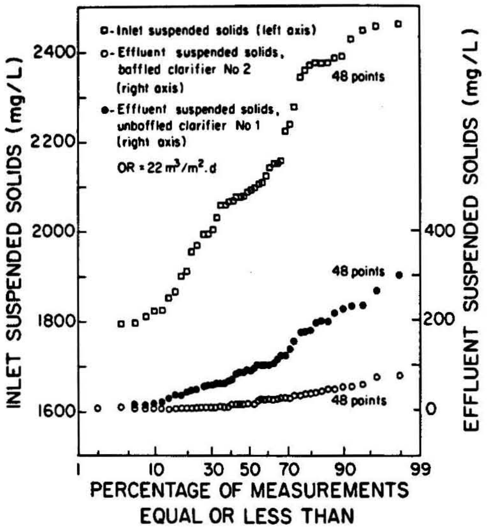


Figure 9. Comparison of the performance of parallel paired clarifiers with and without flow contraction baffles at an overflow rate of 22 m³/m² · d for Little River Pollution Control Plant activated sludge mixed liquor.

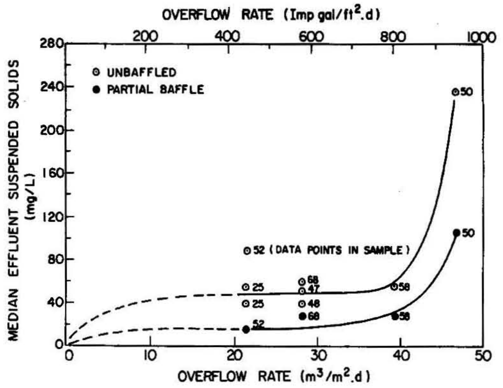


Figure 10. Comparison of overall performance of parallel paired clarifiers with and without contraction baffles for Little River Pollution Control Plant activated sludge mixed liquor.

be seen in the effluent suspended solids. The baffled clarifier has a mean effluent suspended solids concentration of 22 mg/L at 22 m³/m² · d, while the unbaffled clarifier has a mean effluent suspended solids concentration of 104 mg/L (Table 1). Statistical calculations show a highly significant difference in performance of those two clarifiers at the 99% confidence level. At 47 m³/m² · d, the separation is still very large even though the level of solids in the overflow more than doubles. Table 1 shows that flow contraction results in a mean effluent with 162 mg/L while without the baffle the mean reaches 295 mg/L.

The manner of plotting these results, however, in order from lowest to highest, tends to ignore the correlation that exists between effluent suspended solids leaving the twinned clarifiers at a given time. The test results presented in Table 1 likewise ignore this correlated information, even though the statistical results are adequate for present purposes. A test of the data that would make use of the correlated information would be the paired t-statistic made by observing the difference between the paired effluent suspended solids concentrations as a function of time. This was done for tests on raw sewage summarized in Figure 6.

Because of the low suspended solids in the raw sewage influent the 10% to 15% difference in solids removal shown in Figure 6 corresponds to a mean difference between suspended solids in the overflows from the baffled-unbaffled clarifiers of only about 6 mg/L. Even with this small difference using the paired t-statistic (based on concentration differences between the two effluents), it was found to be highly significant.

Perhaps the most dramatic demonstration of the reduction in overflow suspended solids is the visual evidence shown in Figure 11. Overflow from the baffled clarifier is noticeably clearer than that from the unbaffled one.

TABLE 1. STATISTICAL ANALYSIS OF PARALLEL TEST RESULTS ON MIXED LIQUOR FROM AN ACTIVATED SLUDGE AERATOR.

		Effluent Conc. (mg/L)			Difference In Means Significant?		
Overflow Rate (m³/m² · d)	Feed Conc. (mg/L)	Clarif. 1 (no baffle)	Clarif. 2 (no baffle)	Clarif. 2 (with baffle)	No	Yes	Highly
28	x 1965.87	50.979	49.957				
	s —	39.775	27.3448		●		
	n 47	48	47				
22	x 1973.486	71.6133	73.667				
	s —	9.2765	13.199		●		
	n 35	25	25				
47	x 2062.34	294.877		161.877			
	s —	269.754		121.126			●
	n 53	57		57			
40	x 1873.6	116.655		33.517			
	s —	129.477		22.085			●
	n 60	58		58			
28	x 2093.138	128.029		37.706			
	s —	26.802		4.367			●
	n 65	68		68			
28	x 2093.138	61.1		37.706			
	—	35.4026		4.367			●
65		60		68			
22	x 2083.875	104.333		21.5833			
	s —	10.8738		2.7772			●
	n 48	48		48			

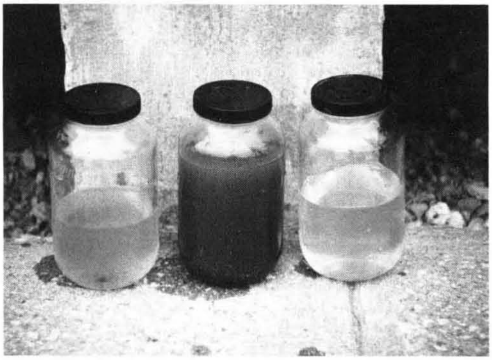


Figure 11. Comparison of overflow samples from baffled and unbaffled paired clarifiers operating in parallel at 28 m³/m² · d on Little River Pollution Control Plant activated sludge mixed liquor: center = influent mixed liquor; left = overflow from unbaffled clarifier; right = overflow from clarifier equipped with a flow contraction baffle.

DISCUSSION

Sludge Behavior

Most of the sludges used had a Sludge Volume Index (SVI) below 120, which means the sludge was well-behaved from a settling and thickening standpoint. Settling flux data for the sludge during various experiments were collected and analyzed. The data show, for example, that at an underflow solids concentration of 4.5 g/L, the limiting solids flux for this sludge would be 105 kg/m² · d. This value, however, is well above the actual loading used at an overflow rate of 22 m³/m² · d. Increasing the hydraulic loading above 64 m³/m² · d brought the solids loading into the range of the limiting solid flux so problems at that overflow level could have been expected.

Operational problems concerned the deposition of sludge on the baffle surface. Because of the size of the baffle, a scraper could not be used on the ledge portion of the baffle. Some sludge collected on this ledge and interfered with grab sample measurements. Thus, it was necessary to scrape the ledge prior to taking a grab sample. Another problem concerned the high sludge level in both clarifiers during the tests. Indeed, at overflow rates above 47 m³/m² · d, the sludge blanket nearly reached the surface of the clarifier and some sludge escaped over the exit weir. However, scum periodically floating up from the sludge blanket near the center of the clarifier was trapped within a floating ring of plastic hose, preventing this scum from interfering with the effluent measurements.

The high concentrations of effluent suspended solids shown in Figure 10 and in Table 1 reflect scaling problems in carrying out experiments on a pilot-scale clarifier, rather than the settling characteristics of the sludge. The scaling problem was discussed with respect to attempts to measure performance at a very high overflow rate.

Comparison of Laboratory and Pilot Plant Data

Laboratory measurements were made only on discrete-settling, non-flocculating solids so these data can be compared only with the primary clarification data. Unfortunately, laboratory measurements were made at lower overflow rates. Figure 12 collects laboratory measurements of Murphy, et al. [8] and Wigglesworth, et al. [9] made with a diatomaceous earth whose particle size was chosen so that its settling characteristics were similar to the settling behavior of raw sewage. Even though the overflow rates were less than half the rate used to obtain the data in Figure 6 so that much higher percent solids removal was obtained, the approximately 10% improvement due to the use of flow contraction seen in Figure 12 agrees well with the improvement measured in the pilot plant.

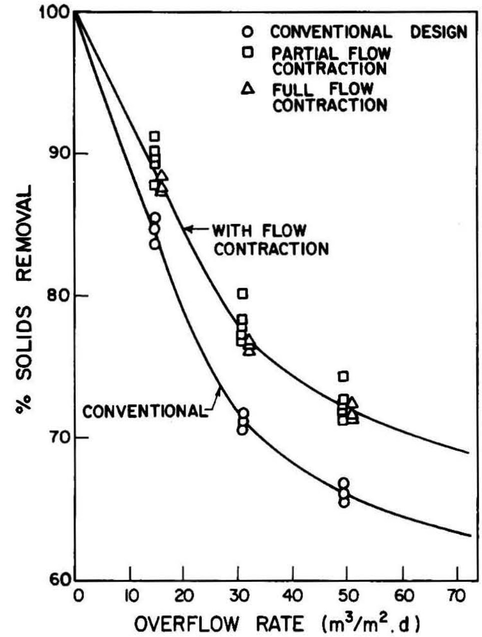


Figure 12. Comparison of the performance of baffled and unbaffled 1.2 m circular clarifiers with a diatomaceous earth. Full and partial baffling are illustrated in Figure 3.

It is worth noting that the laboratory data include measurements with both full and partial baffles (Figure 3); these data overlap. Only partial baffles were used in the pilot plant measurements; nevertheless, Figure 12 suggests that the improved performance found will apply to full baffles as well.

Comparison of Primary and Secondary Clarification Results

Table 2 summarizes the improvements resulting from the application of flow contraction to secondary clarification. The data indicate larger improvements at low overflow rates, with the exception of the 1984 results, which indicate a large improvement, but less than half that measured in the summer of 1986. It seems likely that a difference in settling characteristics will account for the anomaly. Unfortunately, these characteristics were not

TABLE 2. REDUCTION IN EFFLUENT SUSPENDED SOLIDS RESULTING FROM FLOW CONTRACTION BAFFLE.

Overflow Rate (m³/m² · d)	% Reduction at difference points in probability plots			
	25th%	50th%	75th%	90th%
22	92	82	81	77
28	75	53	44	69
40	59	50	68	80
47	46	50	31	47
20*	20	20	22	22

* Data obtained during winter, 1984.

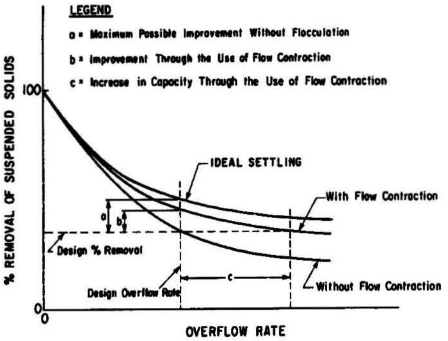


Figure 13. Schematic of percent solids removal versus overflow rate for clarifiers.

measured. The 1984 Little River data agree better with the 25% improvement measured in the Burlington pilot plant for an overflow rate of 29 $m^3/m^2 \cdot d$ than do the 1986 data.

Disregarding differences in the secondary clarification data, it is still evident that flow contraction works a greater improvement with secondary (20 to 80%) than it does with primary clarification (10 to 15%). The reason behind this observation is not known.

Implications for Increased Capacity

Figure 13 is a schematic of the data shown in Figures 7 and 12 where we have removed the limitation imposed by sludge levels. This figure illustrates that the 50% reduction in suspended solids in the effluent translates into a significant increase in the hydraulic capacity of a clarifier, due to the use of the baffle. This is illustrated in the figure by the increment in overflow rate denoted by "c." The large incremental capacity arises from the lower slope of the overflow suspended solids versus overflow rate curve for the baffled clarifier compared to the unbaffled one.

The upper curve indicates the limiting clarifier performance (without chemical flocculation), which is given by quiescent settling. As discussed by Murphy, et al. [*8*] and Silveston and Hudgins [*13, 14*], flow contraction causes clarifier performance to approach the quiescent settling limit.

Because flow contraction appears to be particularly effective with secondary effluent, reducing the suspended solids to 25%–80% of that conventionally obtained even at the highest overflow rate used, the significance of Figure 13 is that the flow capacity of many presently overloaded secondary clarifiers, if retrofitted with an appropriate baffle, can be substantially augmented for a relatively minor investment compared with that of a plant expansion.

CONCLUSION

When applied to secondary biological waste treatment, the flow contraction baffle improved the removal of suspended solids from an activated sludge mixed liquor by 50% or more compared to a conventional clarifier. This result agrees with a body of evidence from other pilot- and bench-scale studies that demonstrate that flow concentration baffles substantially improve a liquid-solid separation for both primary and secondary clarification. Sludge build-up problems at the pilot scale clearly show that any further demonstration of the flow contraction baffle must be done in a full-sized plant.

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Low Temperature Thermal Treatment (LT^3) of Volatile Organic Compounds From Soil: A Technology Demonstrated

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Weston has developed, tested, demonstrated, and operated a transportable system to remove, through evaporation, and subsequently destroy volatile organic contaminants in soil and sludges. The process is called Low Temperature Thermal Treatment (LT^3). The purpose of this patented process is to restore the soil to its original condition, making it suitable for on-site backfill and to eliminate the long term liability and potential costs associated with off-site transportation and disposal.

INTRODUCTION

Weston has developed, tested, demonstrated, and is currently operating a patented process to remove, through evaporation, and either destroy or recover volatile organic compounds (VOC's) from contaminated soils. We have named this system LT^3—Low Temperature Thermal Treatment. The purpose of this patented process is to restore the soil to its original condition, making it suitable for on-site backfill and to eliminate the long-term liability and potential costs associated with environmental problems.

There is an existing problem of immense magnitude associated with the underground storage of liquid fuels and other volatile organic compounds. Many of the more than 2 million underground storage tanks in the U.S. are known to be leaking or to have previously leaked and have since been taken out of service. Estimates put the number of tanks currently leaking at well over 200,000. Estimates indicate as many as 25% of the installed tanks in some regions may be leaking.

Weston addressed this problem with transportable process equipment that can be mobilized to economically address the problems of medium to large environmentally endangered sites. Smaller sites, such as individual tanks at gasoline stations, with only minimal quantities of contaminated soil can most cost effectively be addressed using conventional dig and haul methods. However, as regulations evolve and off-site landfill alternatives become more limited and more costly, LT^3 may become economically viable for even these smaller sites.

In developing the LT^3 system, Weston utilized three different thermal processors, each of a different size and capability. A bench-scale unit with a capacity of 15 lbs/hr (33 kg/hr) was initially used to evaluate the concept. This led to a pilot unit with a capacity of 150 lbs/hr (331 Kg/hr) that was used in initial field tests. Finally, a full-scale production unit with a capacity of 15,000 lbs/hr (33,075 Kg/hr) was built, and is now commercially available through Weston Services, Inc. (WSI).

The LT^3 system is first operated in Springfield, Illinois, where it was used to clean-up soil contaminated as the result of leaking gasoline and No. 2 fuel oil storage tanks. A photograph of the LT^3 site is presented in Figure 1.

The basic pilot system used in the original field tests had a hot oil system, the thermal processor, and an afterburner. The afterburner can be replaced with a condenser and a carbon absorption system to recover the volatiles if economics so dictate. However, the most cost-effective solution is typically to destroy the VOC's in an afterburner.

The full-scale system shown in Figure 2 is straightfor-

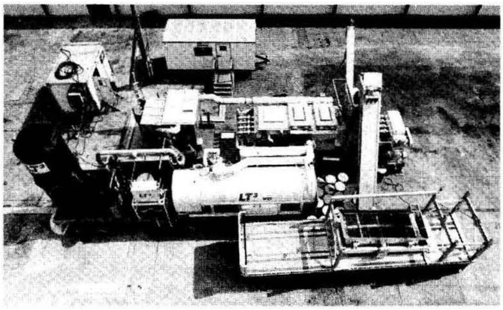

Figure 1. Full Scale LT^3 system installed and operational in Springfield, IL.

ward and relatively simple with four major systems:

- The Solids Handling System
- The Hot Oil System
- The Gas Handling System
- The Water System

This production unit is designed to process 15,000 lb/hr (6,804 Kg/hr) of contaminated soil with a moisture content of 20% and a 1% concentration of VOC's. These are design parameters, but the system can process a wide variety of soils with differing moisture and contaminant concentrations. The system is comprised of equipment assembled on three flat-bed trailers and requires an area of about 75 feet (23 meters) square.

SOLIDS HANDLING

Contaminated soil is excavated and stockpiled for feeding into a scalping screen to remove oversize (+2 inch) (51 mm) material and debris. Screened material is transported by an enclosed drag conveyor to a hopper that directly feeds the thermal processor. The thermal processor is an indirectly heated auger type heat exchanger for solids and slurries. The processor mixes, conveys, agitates, and heats the contaminated soils allowing the moisture and volatiles to vaporize and escape from the soil. An indirectly heated processor was chosen to eliminate contamination of the heating medium and to improve thermal efficiency.

The low operating temperature of the processor, approximately 400°F (204°C), minimizes the thermal load compared to incineration and still allows vaporization of the volatiles. Not only is less heat required to process the volatiles, but the soil matrix does not have to be heated to incineration temperatures.

The processor resembles a jacketed screw conveyor, with four parallel screws contained in a single jacketed trough. The shaft and screw flights are also hollow to allow the hot oil to be circulated through the shaft and flights as well as the jacket. This type of processor has been used for over 30 years to dry, heat, and cool a variety of materials, and is especially popular for drying products in the mineral industry due to its rugged construction, versatility, and reliable performance. These are the same attributes that make it an ideal component for use in the Weston system where reliability and the capability to process varying types of soils is essential.

In the portable system two thermal processors, each

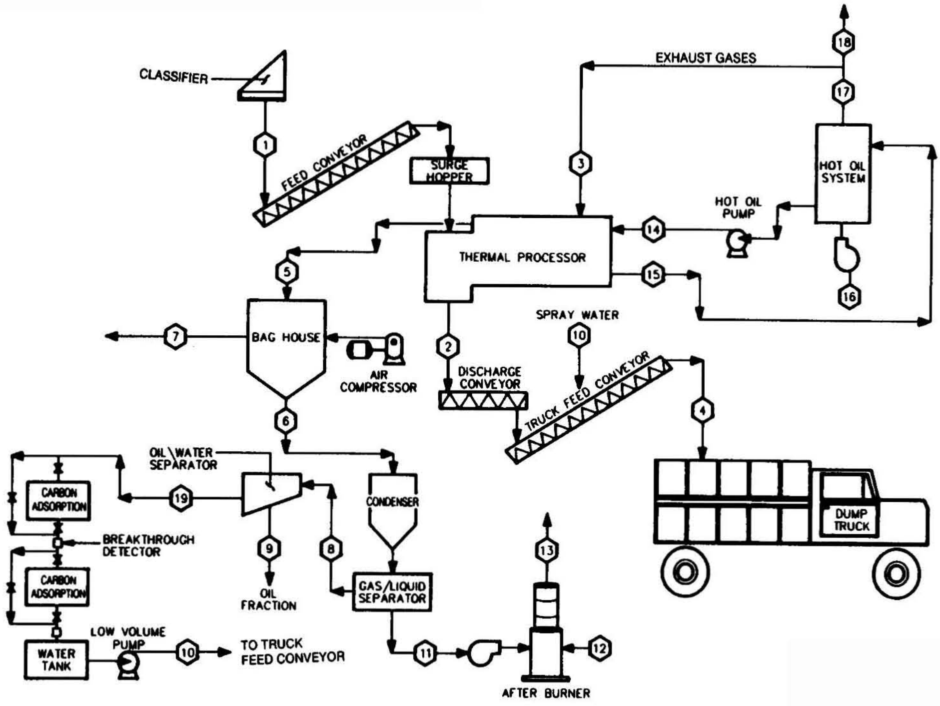

Figure 2. Process schematic mobile low temperature thermal treatment (LT^3) system.

TABLE 1. RESULTS OF PREVIOUS BENCH-, PILOT- OR FULL-SCALE LT^3 PROJECTS

Date: July 28, 1988
Client: Confidential
Location: Springfield, IL
Description: Full-Scale Clean-Up of No. 2 Fuel Oil/Gasoline Contaminated Soil
Processed Soil Temperature: 350°F
Processed Soil Residence Time: 70 Minutes

Contaminant	Boiling Point (°F)	Feed Soil Concentration (ppb)	Processed Soil Concentration (ppb)	Contaminant Removal Eff. (%)	Concentration in TCLP Leachate (ppb)
Benzene	176°F	1,000	5.2	99.48%	(Not Analyzed)
Toluene	213°F	24,000	5.2	99.98%	(Not Analyzed)
Xylene	291°F	110,000	<1.0	>99.999%	(Not Analyzed)
Ethyl Benzene	277°F	20,000	4.8	99.98%	(Not Analyzed)
Napthalene	424°F	4,900	<330	>93.3%	(Not Analyzed)
Carcinogenic Priority PNA's					
Benz(a)anthracene	850°F	<6,000	<330	<94.5%	16J
Benzo(a)pyrene	923°F	<6,000	<330	<94.5%	4J
Benzo(b)fluroanthene	896°F	<6,000	<330	<94.5%	N/D*
Chrysene	875°F	<6,000	590	<90.2%	N/D*
Dibenzo(a,h)anthracene	975°F	<6,000	<330	<94.5%	N/D*
Non-Carcinogenic Priority PNA's					
Acenapthene	534°F	890	<330	<62.9%	1J
Acenapthalene	518°F	1,200	<330	<72.5%	0.13J
Anthracene	644°F	2,700	<330	>87.8%	3J
Benzo(g,h,i)perylene	995°F	<6,000	<330	<94.5%	N/D*
Benzo(k)fluroanthene	896°F	<6,000	450	<92.5%	N/D*
Fluroanthene	707°F	<6,000	<330	<94.5%	N/D*
Fluorene	560°F	4,900	<300	>93.3%	N/D*
Ideno(1,2,3-c,d)pyrene	950°F	<6,000	<330	<94.5%	N/D*
Phenathrene	644°F	2,400	430	82.1%	3J
Pyrene	759°F	<6,000	<330	<94.5%	N/D*

Notes:
N/D* — Not Detected. Detection Limit = 20 ppb.
"J" — Present at Less Than Detection Limit.

with four, 18" (457 mm) diameter, 20 foot (6,096 mm) long screws have been mounted in a piggyback fashion. They are operated in series to insure adequate residence time and agitation to release even volatiles trapped in the interstices of the soil matrix. After processing, the soil is transferred via enclosed screw conveyors to a dump truck for stockpiling or use on-site as backfill.

HOT OIL

The heating system for the hot oil is a conventional closed loop 6 million Btu/hr (1.76 million J/S) hot oil heater with the associated pumps, tanks, piping, and valves. This system heats the oil to 650°F (343°C) and can be fired on propane, natural gas, or oil. The oil temperature and flow rate can be adjusted to compensate for varying conditions. Heat is provided to the soil by circulating hot oil through the hollow flights of the screws and the passages in the trough jacket.

GAS SYSTEM

The vaporized contaminants are swept from the thermal processor using a sweep gas mixture of air and exhaust gases from the hot oil system. The oxygen content in the sweep gas is controlled by the quantity of exhaust gases from the hot oil system. This not only provides a more thermally efficient system, but also provides safety by controlling the process gas atmosphere at an oxygen level below the lower explosive limit.

This sweep gas carries the volatiles through a fabric filter (baghouse) for particulate emissions control and then into a condenser. The condenser reduces the water load on the subsequent afterburner and condenses the volatiles, making it possible to recover the volatiles if desired.

Water

Condensate from the condenser is composed of water and condensed volatile organics. The two-phase condensate is separated in an oil/water separator. The separated oil is stored in 55 gallon (208 liter) drums for future transport and processing off-site.

The water, with a relatively low concentration of soluble organics, is treated in a two-stage carbon absorption system. The clean water is sprayed on the discharging solids to cool the processed soil and to suppress dust formation. The system can be modified to include a caustic wet scrubber for removal of sulfides and chlorides if a potential of emitting these in excess of the applicable codes exist.

RESULTS

In the pilot program at Letterkenny Army Depot under a contract with the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Weston evaluated the processor performance against controlled test variables, including residence time, soil discharge temperature, and air inlet temperature. Moisture content and the level of contamination varied with the material to be processed. The results were favorable and can be summarized by stating:

- LT^3 is an effective technology for removing VOC's from soil.
- Greater than 99.9% VOC removal from the soil was demonstrated.
- Stack emissions were in compliance with Federal and state regulations, including those for VOC's, HCl, CO, and particulates.

The pilot work led to further investigation of the versatility of the system and its capability to process a variety of contaminants in a variety of soils. We undertook a series of bench-scale tests on a smaller processor (3 feet long) (914 mm) testing these contaminants: No. 2 fuel oil, leaded and unleaded gasoline, JP-4, and VOC's (TCE, DCE, PCE, and Xylene). We also tested chlorinated benzenes with positive results. Column leach tests of the processed soil showed less than 12 ppm of chlorinated benzene compounds and heavy metal concentrations two orders of magnitude below the EP toxicity action levels.

We continue to use the bench-scale equipment to predict the expected capability of the full-scale unit to process a given soil matrix with specific contaminants. This way we can avoid mobilizing the equipment and inappropriately using the LT^3 system to solve a problem that cannot or should not be processed by this system.

The encouraging results of both bench-scale testing and the pilot program at Letterkenny provided the confidence for Weston Services to invest in the construction of a full-scale system. This system first operated in Springfield, Illinois, on soil contaminated with gasoline and No. 2 fuel oil and has now been moved to Oklahoma City to treat soils contaminated with aviation fuel and chlorinated solvents. We have had excellent results to date and the work we have completed provides extensive experience. Results of the project in Springfield, Ill. are shown in Table 1.

This technology provides a less expensive method to clean soil contaminated with VOC's and allows the soil to be reused for backfill of a new tank. Use of this system eliminates the need for hauling contaminated soil to a special waste landfill, with all the attendant problems including manifesting and long term liability.

Costs for this process vary with the soil type to be cleaned, contaminant concentrations, and the moisture content of the soil. The most significant factor affecting the overall cost of the cleanup, however, is the volume of material to be processed. To keep unit costs competitive with alternatives such as landfill, the fixed costs of mobilization must be spread over as much soil as possible. Our estimates currently indicate that to be economical a project should have 1,000 yd^3 (765 m^3) of contaminated soil that needs processing. There is no limit to the maximum project size. As the quantity of material to be processed increases, the unit costs proportionately decrease.

Assuming excavation and landfill is technically and legally feasible, the smallest economical project for the LT^3 system may be a larger service station with fairly extensive contamination due to one or more leaking tanks, or more likely a refueling depot or distribution center where there is enough soil to be processed to offset the fixed mobilization costs.

For VOC contaminated soils, the LT^3 system provides an alternative to excavation and transport to a special waste landfill with all the attendant manifest problems and future potential liability.

LITERATURE CITED

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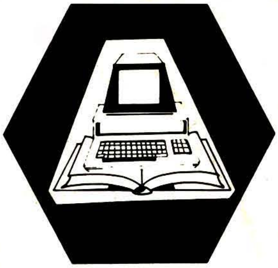

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