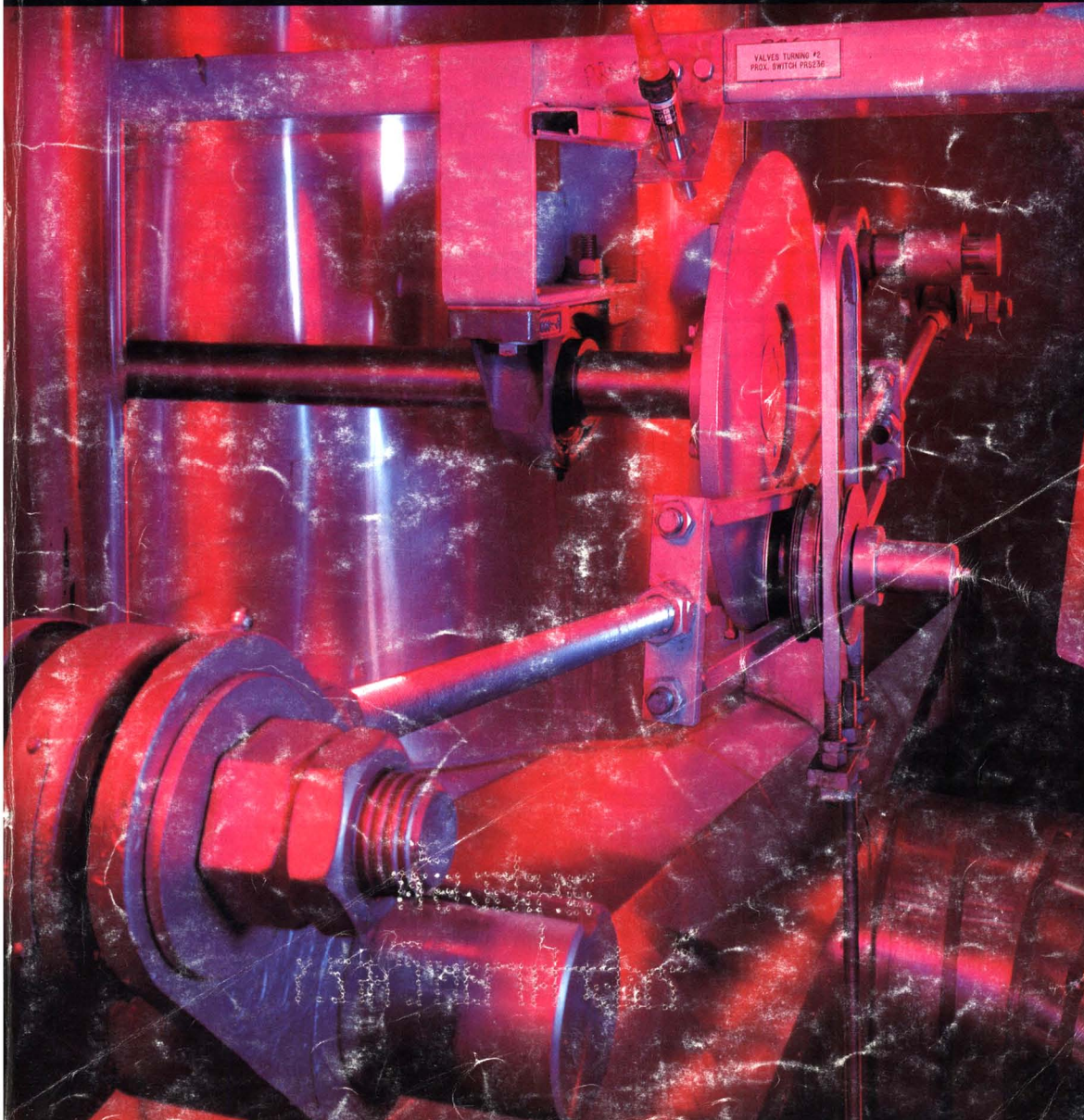
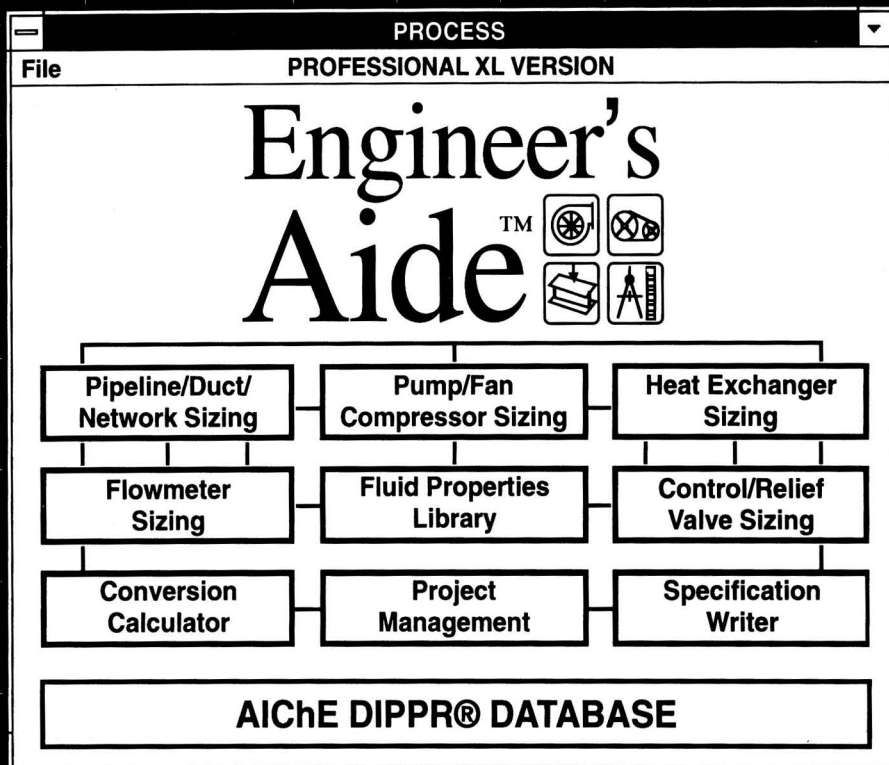


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Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multifaceted aspects of the pollution problem. It will provide thorough coverage of abatement, control, and containment of effluents and emissions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

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Cover: Wheelabrator Clean Air Systems/HES patented drive valve system (see page A5). Photo courtesy of Wheelabrator Clean Air Systems, Schaumburg, Illinois. Cover Design: Joseph A. Roseti

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Collective Ignorance and Escalating Expectations

Robert D. Mutch, Jr.

It's been 16 years since Love Canal jarringly awoke the nation and, to some extent, the world to the risks posed by past disposal of industrial wastes on land. It's been 14 years since Superfund was hastily passed in the fleeting moments of the Carter Administration. The understandable outrage of a citizenry, until then blissfully ignorant of the inevitability of waste generation in an industrial society, is still present but shows signs of weakening in the face of a prolonged economic downturn and, I think, more importantly, in response to a slowly evolving understanding of history—specifically the history of waste disposal practices and the associated environmental consequences. A federal judge recently struck down the U.S. Department of Justice's and New York State's efforts to extract \$250 million in punitive damages from Hooker Chemicals and Plastics Corporation (now Occidental Chemical Corporation) in connection with the Love Canal case, concluding that:

Hooker's decision to landfill its chemical wastes, its choice and maintenance of the site, and its method of disposal operation all comported with the available knowledge and industry practice of the time.

Similarly, the judge decided that it was necessary to judge Hooker's actions in

light of contemporaneous industry practice of solid waste disposal, the existing regulations, and recommendations made by governmental agencies, and the state of knowledge of the dangers of chemical landfills...

It is tempting for people, especially those new to the environmental field, to join in the bashing of industry for perceived crimes against our environment. America loves an unambiguous

enemy and has responded powerfully and unflinchingly when confronted with such enemies in the past. Industry has assumed that type of unambiguous role, often with only half-hearted protestation, and has suffered the consequences. But ever so slowly, and much to the annoyance of some zealots, ambiguity is seeping in, carrying with it the doubt that perhaps industry is not singularly responsible for all our past waste disposal woes, that perhaps scientists, engineers, politicians, and government regulators all had a hand, to one degree or another, in the creation of this waste disposal legacy.

For example, consider the following disposal practices:

- Landfilling wetlands with undiked municipal and industrial waste.
- Dumping municipal and industrial solid waste in unlined, abandoned sand and gravel pits.
- Co-mingling millions of gallons of solvents in unlined municipal solid waste landfills.

Are the above practices environment crimes today? Absolutely. Yet as recently as 15 to 30 years ago, not only were these practices not crimes, they were fully sanctioned by regulatory agencies. Landfilling of wetlands was not only sanctioned by regulators, it was encouraged. The U.S. Public Health Service, in its landmark 1939 study of several New York City landfills, concluded that "filling is one of the best methods of rat and mosquito control for swamps and marshes." This philosophy prevailed up until the 1960s. Abandoned sand and gravel pits—one of the worst hydrogeologic regimes for a landfill—were extensively used for landfills in the 1940s, '50s, and '60s. Why? Because it was mistakenly believed that even permeable sand and gravel could protect underlying groundwater if the landfill was merely maintained a suitable distance above the groundwater table (usually three to five feet) and the landfill was properly operated. While liquids are an anathema in landfills today, less than twenty years ago unlined landfills were routinely permitted to commingle liquid industrial waste with municipal solid waste.

Two conclusions emerge from a thorough review of the history of waste management in the U.S. First, for the bulk of this

Robert D. Mutch, Jr., Ph.D., P.E. is a principal of Eckenfelder Inc., in Mahwah, New Jersey. He has twenty-two years of experience in the environmental field with emphasis on the design and remediation of waste disposal sites. He is also an adjunct professor of hydrogeology at Manhattan College in Riverdale, New York.

century we were profoundly ignorant of the possible consequences of waste disposal on land. Moreover, it was principally this nearly universal ignorance, not criminal intent or reckless disregard for the environment (although there is some of that too), on the part of scientists, engineers, politicians, and environmental and public health regulators that led to our current dilemma. We naively viewed the subsurface as possessing an almost inexhaustible capacity to absorb, filter, and attenuate waste materials entering it. In actuality, the earth's assimilative capacity is quite limited, especially for attenuating manmade chlorinated solvents like trichloroethylene or methylene chloride (But then most practicing engineers and hydrogeologists didn't even know what trichloroethylene or methylene chloride were until the mid-1970s when gas chromatography became more widely available as an analytical tool).

The second conclusion relates to expectations. As our tolerance for pollution in general, and groundwater contamination in particular, diminished over time, our expectations for the performance of waste management practices correspondingly escalated. For example, consider the beleaguered sanitary landfill. Up until the mid-to-late 1970s, landfill designs were typically predicated upon the principle of "natural attenuation," wherein leachate from a landfill was to be absorbed and attenuated by the natural geologic and hydrologic system. In other words, landfills were originally designed to leak, but hopefully in a way that aquifer contamination would be of modest proportions and existing water supplies would not be endangered. Later, however, as tolerance for pollution diminished, many of these very same landfills were suddenly expected to preserve virtually natural groundwater quality at their waste boundaries. Predictably, few landfills could achieve this bit of legerdemain and were either forcibly closed or voluntarily shut down operations.

Escalating expectations are fine and undoubtedly necessary to advancement of the state-of-the-art. However, in the U.S. these heightened expectations have an ugly side. Instead of promoting future waste management advances, some people, presumably caught up in the well-meaning enthusiasm of the environmental

movement, are fixated on the past. Their potentially productive energies are dissipated condemning and vilifying all those companies and individuals that failed to historically manage wastes in accordance with current standards. As the title of this journal heralds, we have made tremendous environmental progress, especially in the last 20 years. Let us take due pride in that progress and not look condescendingly at or, worse, condemn the evolutionary steps we took along the way. It's not progress if you haven't advanced from some less-accomplished position.

Even though the frontiers of environmental science are currently expanding with unprecedented speed, we need to look back from time to time at our history, not with condescension or scorn, but in search of understanding and perspective. The past is important in many areas of the environmental field. It plays a pivotal role in the monumental legal battles being waged all across the country between insurance companies and those firms they insured over the issue of soil and groundwater contamination and, specifically, who should pay for cleaning it up. At the heart of this litigation lies the question "Should the soil or groundwater contamination and the liabilities resulting from a certain disposal activity have been *expected or intended* at the time the activity was undertaken?" One cannot begin to answer this question without an appreciation of the historical evolution of waste disposal practices and associated knowledge. A knowledge of waste management history could help quell the sometimes bitter discourse between regulators and the regulated. I also believe that a wider understanding of this history is necessary if we are to advance beyond the recrimination, finger-pointing, and resulting legal morass which characterizes our current foundering cleanup efforts. We need to realize that we are all responsible, to one degree or another, for the problems of inadequate past waste disposal and, consequently, we must find a way to equitably bear the burden together. It is hard to imagine a more fitting assessment of the causative factors behind our current waste site cleanup crisis than the declaration of Walt Kelly's cartoon strip character, Pogo: "We have met the enemy and he is us."

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A number of Chemical Engineers have been hired under the Environmental Protection Agency's Senior Environmental Employment (SEE) program to work on pesticides. The Senior Environmental Employment program (SEE) is administered by the EPA. The Program is authorized by the Environmental Programs Assistance Act of 1984. This Act provides opportunities for senior citizens needing some financial support to supplement their retirement and to contribute to a better environment.

While the work is considered part-time, it is not unusual for participants to work 40 hours a week. The program is being used throughout EPA as ten percent of their workforce. However, no SEE person is expected to handle the responsibility of federal employees.

Chemical engineers can begin as level 4 employees under the SEE program. Wages are \$10.50 per hour increasing \$0.50 per hour after the first year of employment. Benefits include paid vacation, holidays and sick days plus health insurance (depending on the number of hours worked per week).

No special funding is available for hiring SEE personnel. The EPA unit (program office or regional office) must have the necessary funding in their budget. Once they determine there is a need, a job description is prepared which is distributed to SEE program grantees. The grantees are: American Association of Retired People; National Caucus Center on Black Aged; National Council of Senior Citizens, National Association of Hispanic Elderly, National Asian Pacific Center on Aging and the National Council on the Aging.

Interested engineers should forward their resumes periodically to the grantees. Resumes can also be forwarded to the EPA Laboratories and the EPA Regional Offices.

Addresses and contact names are available from AIChE's Member Employment Services Department, 345 East 47 St., New York, N.Y. 10017. (212) 705-7523 • FAX (212) 752-3294.

AIChE Summer National Meeting to Highlight Environmental Issues

The theme of the four day AIChE Summer National Meeting which will take place August 14 through 17 at the Marriott City Center in Denver Colorado is "Stewardship of the Environment." The majority of the program sessions will focus on environmental concerns.

A plenary lecture to be given by C.L. Gray, Jr., EPA director of regulatory programs and technology, on the topic "Fuels for the 900s and Beyond" is listed among the conference highlights. Also listed is the Fifth Annual Pollution Prevention Topical Conference a regular feature of the AIChE Summer Meeting. The Topical Conference offers five sessions on current and future pollution prevention strategies.

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Environmental Considerations in Process Design and Simulation

Prepared by J. Eisenhauer and S. McQueen, Energetics Inc.

The Environmental Protection Agency, The Department of Energy, and The Center for Waste Reduction Technologies, brings a new publication which identifies how environmental factors should be incorporated into process simulation and design tools for the chemical process industries.

Authored by leading U.S. experts drawn from the industrial user community, software designers, university researchers, and federal R&D managers—this publication identifies the important R&D needed in the process simulation area and offers some perspective on R&D priorities. Ideas range from new theoretical modeling approaches being pursued in the academic community to the pragmatic data needs of process engineers who must find ways to meet environmental regulations for current operating facilities.

Issues and R&D needs addressed:

- The pertinent environmental considerations and how they should be brought into the optimization/design process
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Washington Environmental Newsletter

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

REFORMULATED AND OXYGENATED GASOLINES

It may be time to dust off those old slide rules off, at least perfect a new computer program to figure out the amount "renewables" that will need to be purchased, and put into summertime reformulated gasoline. If you haven't heard, EPA has blended politics with gasoline to develop what some at EPA have dubbed as the "Roxy" program; but first a bit of background.

When the Congress enacted the Clean Air Act Amendments of 1990 (CAAA) it included provisions that require refiners and other suppliers of gasoline to alter the composition of gasoline distributed in areas where carbon monoxide and ozone pollution are major problems. For carbon monoxide, the CAAA requires the use of oxygenated gasoline in 39 cities. For ozone nine cities specified in the law and a number of other areas that have voluntarily opted into the program are required to use reformulated gasoline during the summer months. (See Table I at the conclusion of this article for a listing of all areas in the country that are either required to use reformulated gasoline or that have opted into the program.)

The 39 city oxygenated gasoline program went into effect in the winter of 1992. The nine-city summertime reformulated gasoline program becomes effective January 1, 1995. Both fuels, reformulated and oxygenated gasolines must contain a specified percentage of oxygen in the form of an oxygenated compound. The most predominate oxygenates are ethanol and methyl tertiary butyl ether or MTBE. Others that are less abundant are other ethers including ethyl tertiary butyl ether or ETBE. In the 39-city program, oxygenated gasoline must contain at least 2.7 percent oxygen by weight and in the nine cities plus the opt ins, reformulated gasoline must contain no less than 2.0 percent oxygen by weight. The following chart shows the respective volume percentage of three oxygenates needed to get to the 2.0 and 2.7 weight percent requirements.

Oxygenate	2.0%	2.7%
Ethanol	5.7%	7.7%
MTBE	11.0%	14.9%
ETBE	12.7%	17.1%

Just as industry got those slide rules working and the computers programmed to comply with these requirements EPA added a new dimension to an already complex situation. As a result of a recently promulgated rule, EPA is now mandating that effective January 1, 1995, 15% of the oxygen used by refiners and other suppliers of reformulated gasoline be derived from renewable sources such as "corn, other grains, biomass and even garbage," i.e., renewable oxygenates or "Roxy". EPA defines nonrenewables to include oxygenates made from fossil fuels, such as petroleum or natural gas. MTBE is considered nonrenewable unless it is derived from garbage generated methane. In 1996 and beyond this 15% requirement increases to 30%.

The areas where reformulated gasoline is required represent 35% of all of the gasoline sold in the U.S. The renewable requirement is 30% of the 2.0 weight percent oxygen requirement of reformulated gasoline so the volume of oxygenate used depends on the oxygenate(s) selected. As there is less ethanol needed to meet the 2 weight percent target there is a bias towards this oxygenate. However, there is a catch. Ethanol used in reformulated gasoline during the summer months, or ozone period, can not be counted towards the 30% renewable mandate. Adding ethanol to gasoline raises the Reid Vapor pressure about 1.0 psi and increases hydrocarbon emissions, which adds to ozone formation.

To compensate for this EPA has added a credit trading program and annual averaging. In other words ethanol used in the wintertime in oxygenated gasoline, in carbon monoxide nonattainment areas that are also summertime reformulated gasoline areas (we refer to them as overlapping areas - see Table 2 for a list of these areas) can be credited towards the 30% renewable oxygen mandate for reformulated gasoline. Also refiners, and others, who use a lot of ethanol in the wintertime, in these overlapping areas can generate credits that can be traded or sold to others that are not able to meet their renewable oxygen requirements. Credits trading and averaging are also enhanced if a refiner supplies reformulated gasoline in the nine plus areas beyond the summer ozone season. Unknown is what could happen in the market if no one generated renewable oxygen credits or makes allowances for averaging.

This recent ruling by EPA is very controversial. It was opposed by the oil industry and the environmental community. (The American Petroleum Institute and the National Petroleum Refiners Association have filed suit challenging EPA's decision and are seeking to block implementation of the rule pending a court review of the merits of the API/NPRA case.) Support for the rule came from the farmers, who are hoping for higher corn prices and the ethanol producers such as Archer Daniels Midland. There was also very strong support from many members of congress who represent states where corn is produced. As stated by those opposing the renewable oxygen mandate; the political reality is that corn is grown in more states than oil is produced.

Additional information as well as a copy of this rule can be obtained on EPA's OAQPS Technology Transfer Network Bulletin Board System (TTNBBS). TTNBBS can be accessed with a dial-in-phone line and a high-speed modem by calling (919)541-5742. The parity of the modem should be set to none, the data bits to 8, and the stop bits to 1. Either a 1200, 2400, 9600, or 14400 baud modem should be used. If you have questions about the rule contact our Washington, DC office at (202) 962-8690.

Table 1. List of Reformulated Gasoline Areas

Mandated Areas	Opt-In Areas
New York, New York	Connecticut: entire state
Metro Los Angeles	Delaware: entire state
San Diego, California	District of Columbia
Metro Chicago/Gary Area	Kentucky: Louisville and Cincinnati suburbs
Metro Milwaukee/Racine Area	Maine: Lewiston, Portland, Bar Harbor, Lincoln-Knox counties
Baltimore, Maryland	Maryland: Washington suburbs
Hartford, Connecticut	Massachusetts: entire state
Houston, Texas	New Hampshire: Lawrence, Dover, and Manchester
Philadelphia, Pennsylvania	New Jersey: Allentown-Bethlehem Suburbs Atlantic City, Trenton, and New York suburbs
	New York: Albany, Schenectady, Troy, Buffalo, Niagara Falls, and Long Island area
	Pennsylvania: Pittsburgh, Reading, Allentown, Erie, Harrisburg, Johnstown, Lancaster, Scranton-Wilkes Barre, York, and Sharon
	Rhode Island: Providence
	Texas: Dallas-Ft. Worth
	Virginia: Washington suburbs, Richmond, Petersburg, Norfolk, Virginia Beach, and Newport News
	Wisconsin: In April 1994 the Governor opted- in Kewaunee, Manitowoc, and Sheboygan Counties.

Table 2. Overlapping Areas

State	Nonattainment Area
California	Chico Lake Tahoe (north Shore) Los Angeles (SCAB, Included with LA) San Diego (Included with LA)
Connecticut	Hartford-New Britain-Middletown New Haven-Meriden-Waterbury (NY)
Maryland	Baltimore Washington D.C. (Metro)
New Jersey	N.Y.-No. N.J.-L. Isl. Phil.-Camden Co.
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Recycling and Incineration: Evaluating the Choices, Richard A. Denison and John Ruston, Island Press, Washington, D.C., (1990) 322 pages [ISBN No.:1-55963-055-8] U.S. List Price: \$34.95.

This book compares the recycling and incineration options for the management of municipal solid waste. Landfills take the majority of the 160,000,000 tons of municipal solid waste that is generated annually in the United States. For completeness, the landfill option should have also been included in the comparative analysis in the book.

The beginning chapters introduce the extent of the municipal solid waste problem in this country and the focus on waste reduction as the highest priority. For example, consumers pay more for packaging food than farmers receive for producing it. The waste characterization discussion leading to economic comparisons is particularly well presented. Several interesting case studies for recycling and incineration proposals in major metropolitan areas are included.

The book then proceeds to health and environmental risks of incineration, while retaining incineration as an integral part of a total waste management program. Volume and toxicity waste reduction through source reduction, separation, and recycling should be practiced first with incineration as a viable option for the residual combustible wastes. There is an interesting discussion of incinerator ash characterization and disposal, followed by the control of incinerator air emissions. The recycling of these byproducts was not discussed. The chapter on risk assessment was well conceived and written.

The remainder of the book is devoted to strategic planning for municipal solid waste management from the perspective of the public. The decision of a local community on an incinerator proposal is an emotional and controversial issue. This book provides constructive insight for local citizens faced with this dilemma.

In summary, I found the book to be useful in better understanding logical options for the management of municipal

solid waste. This book is recommended for people from the public, industrial, and government sectors alike.

Charles A. Wentz, Jr., Ph.D.
Associate Dean
The Petroleum and Petrochemical College
Chulalongkorn University
Bangkok, Thailand

Fighting Toxics: A Manual for Protecting Your Family, Community, and Workplace,

Gary Cohen and John O'Connor, Island Press, Washington, D.C., (1990), 346 pages [ISBN No.:1-55963-013-2] U.S. List Price: \$31.95.

This book was written to assist the public in better understanding the need for pollution prevention rather than pollution control. It outlines strategies about how citizens can prevent pollution locally, thus influencing the economic and environmental health of their communities.

Synthetic toxic chemicals are described as the nation's number one hidden health problem. These synthetic chemicals are characterized as "very dangerous, largely untested". Since chemical products and processes have created this crisis, the solution lies in changing what is produced and how it is produced.

The utility of this book will vary with the desires and purposes of the reader. It is a useful book for industrial personnel to gain a better understanding of how to be a better corporate citizen and how to satisfy the needs of the public regarding chemical manufacturing and facility siting. On the other hand, it is a useful checklist for the "not in my backyard" (NIMBY) activists who oppose chemicals industrial expansion.

The book begins with defining the toxics crisis in terms of the numerous hazardous waste sites in the United States. A toxics bill of rights for protection of public health is provided, which expands upon community and employee right-to-know legislation and regulations.

Strategies on how to organize and campaign against toxic chemicals are out-

lined. There is a chapter devoted to obtaining information about a company's operations and pollution generation. A detailed format for neighborhood inspections of company facilities and waste dumps is presented. Guidelines on working with the news media are furnished. There are also several chapters about environmental laws and how to effectively use them to further the goals of the reader.

Finally, pollution prevention is stressed as the preferred environmental solution. The problems associated with pollution control are brought into focus. These are contrasted with the benefits of preventing pollution.

I found this book stimulating and worthwhile for readers who are interested in broadening their perspectives in the complex field of environmental protection.

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Handbook of Leak, Spill and Accident Release Prevention Techniques,

R. Noyes, Noyes Data Corporation, Park Ridge, NJ, (1992), 487 pages [ISBN No.:0-8155-1296-1] U.S. List Price: \$76.00.

The purpose of this book is to provide technical guidance to industrial personnel to aid in their preventing leaks, spills, or other accidental release from fixed facilities that produce, store, or transfer hazardous chemicals. To that end, the author discusses both fugitive emissions and spills/leaks.

Both of the above topics are extremely important to chemical plant operations. The latter area (spills) has been of major concern for several years. The former (fugitive emissions) has been thrust into the limelight by the Clean Air Act (hazardous chemical provisions) and SARA Title III (emission reporting requirements).

Noyes defines fugitive emissions as the loss of chemicals through sealing mechanisms separating process fluids from

the atmosphere. Included in this category are: valves, pumps, compressors, pressure relief devices, open-ended valves or lines, sampling connection systems, and flanges and other connections used in a processing plant.

The book has fifteen chapters with titles noted below:

1. Regulations and Codes
2. Process Hazardous Control
3. Equipment Hazards Control
4. Secondary Containment Controls
5. Aboveground Storage Tanks
6. Underground Storage Tanks
7. Material Transfer/Loading/Unloading
8. Dust Control
9. Wastewater Emissions Control

10. Facility Spill and Leak Prevention Practices
11. Plant Siting and Equipment Layout
12. Detection and Warning Systems
13. Monitoring VOC Emissions
14. Estimating Emissions of VOCs and VHAPs from Equipment Leaks
15. Prevention Techniques for Selected Major Toxic Chemicals

Although I have read many books on spill prevention, this book is the first addressing leak prevention and it contains much useful information gathered in one place.

My major criticism with this book is that the references are not extensive and are mainly limited to other Noyes Data Corporation and U.S. EPA reports. Indeed, I suspect the book was created by extracting from the above-cited references and combining the material into the text (although I could be wrong on this point).

I do, however, feel this is a useful book and recommend it to the targeted audience (according to the author, this audience should be comprised of plant engineers and managers).

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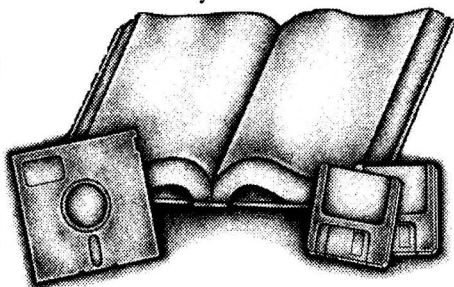
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Software for Estimating Air Emissions of Organic Compounds from Wastewater Treatment Plants

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Introduction

Under the Clean Air Act Amendments (1990), stringent control requirements have been placed on all facilities dealing with or processing toxic chemicals. Since the penalties for non-compliance are prohibitive, most of the facilities dealing with toxic materials need to prepare an emissions estimate for conducting dispersion modeling, prepare a risk assessment, and develop control strategies. The facilities are also required to submit an emission inventory on Form R to the state regulatory agencies under the Emergency Planning and Community Right to Know Act of 1986 [1].

The increasing use of computers in the area of emission calculations has led to the development of a number of computer packages for performing specialized tasks which would otherwise have been complicated and tedious, given the nature of the equations and graphs involved [2,3]. These packages are based on algorithms given in manuals prepared by the United States Environmental Protection Agency (US EPA) [1].

This study focuses on the available software for estimating losses of organic compounds from wastewater treatment processes. Three packages (WATER7, TOXCHEM, and BASTE) modeling emissions from wastewater treatment facilities were found during our literature search [4,5,6]. WATER7 is a public domain software developed by the US EPA, TOXCHEM is developed by Enviromega Ltd. (P.O. Box 1249, Burlington, Ontario, Canada L7R 4L8; Phone (905) 689-4410), and the BASTE model is developed by CH2M HILL (1111 Broadway, Suite 1200, Oakland, CA 94607-4606; Phone: (510)251-2888 ext. 2165).

WATER7 may be obtained over the Internet from the Bulletin Board System run by the US EPA, Research Triangle Park, NC [7]. TOXCHEM can be purchased from Enviromega Ltd. for \$1495, and the BASTE model can be obtained from CH2M HILL for \$200 for users of previous versions of BASTE and \$500 for first time buyers. All three models have been used for regulatory work in the US. The programs are designed to run on IBM compatible PCs.

Overview of the WATER7 Program

WATER7 (Wastewater treatment Compound Property Processor and Air Emissions Estimator Program) is a software package used to calculate the emissions of organic compounds from wastewater treatment processes to the air. It consists of analytical expressions for estimating air emissions of individual waste constituents in wastewater treatment, a database listing

many of the common organic compounds, and procedures for obtaining printouts of the emissions estimates.

In the WATER7 program, separate emission estimates are made for each individual compound identified as a constituent of the waste. The emission estimates are based on the properties of the compound and its concentration in the wastewater. To obtain emission estimates, the user must identify the compounds of interest and provide their concentrations in the waste. The compounds may be selected from the database of nearly 900 chemicals, which is provided with the program. Fresh data may be entered for compounds not listed in the database. Estimates of total emissions are made by adding the estimates for individual compounds.

The program requires an IBM-compatible personal computer with at least 520 KB RAM. The program is compatible with color as well as monochrome screens. The program and data files require about 970,000 bytes of hard-disk space. WATER7 can be run from the disk drive if sufficient space is not available on the hard drive.

The user needs to have a working knowledge of wastewater treatment operations and organic chemistry.

The WATER7 program is menu-driven and quite user-friendly. Listed below are some of the prominent features of the program:

- Access to over 878 compounds and their compound-specific data from the database provided in the software.
- Estimate the value of the compound properties that are not available in the database.
- Specify the operating parameters of the wastewater treatment facility.
- Predict the short- and long-term air emission rates from the facility.
- Save and retrieve individual case studies in separate computer files.

The WATER7 main menu is shown in Table 1. It consists of the following items:

- The HELP menu contains information on UNIFAC, the File, Compound, Unit, View and Print menus, as well as general information about the program and its operation.
- The FILE menu allows opening, saving, and renaming of a current or a previously completed study. The file menu also allows the user to set the screen specifications and various other parameters, and to add of a new compound to the database. The new compound is appended at the end of the database, whereas the rest of the database is listed in alphabetical order.

- The COMPOUND menu provides for selection of up to 20 compounds for analysis. The compound data can be revised, checked for completeness, or used to compare estimates of compound properties from different sources.
- The UNIT menu allows the user to specify the type and the parameters of the wastewater treatment plant. The concentrations of the compounds in the influent, the dimensions of the various treatment units, and the parameters of the impoundment and storage facilities can be specified. The program will supply the default parameters for some of the input parameters. For the rest of the parameters, the user needs to specify the value.
- The VIEW menu is where the results of the various calculations can be accessed. The performance of the wastewater treatment plant, the impoundment facilities and the storage tank can be obtained. The air emissions are given in units of grams/second.
- The PRINT menu presents a print list, and the user can print individual reports for the treatment plant, for each of the impoundment facilities, and for the storage tank. The program does not support PostScript printers. For printing to a PostScript printer, the output should be redirected to a disk file and a word processor or spreadsheet that supports PostScript printers must be used.
- The QUIT menu item allows the user to exit from the program.

Overview of the TOXCHEM Program

The TOXCHEM software package evaluates the fate of toxic organic chemicals and metals in a conventional activated sludge wastewater treatment plant. Volatilization, biodegradation, and sorption to solids are the removal mechanisms handled by this user-friendly, menu-driven model. It has an upgradable database of compounds coupled with extensive context-sensitive help. The program contains five main menu items, namely DATABASE, WASTEWATER, STEADY-STATE, DYNAMIC, and UTILITIES. Each of the menus listed here are discussed below:

- This programs DATABASE menu comprises over 100 toxic contaminants for the purpose of simulating their fate. If the simulation of a compound not listed in the database is required, then one can add to the database by providing information on the characteristics of the compound.
- The WASTEWATER menu contains options for describing the wastewater system. Submenus include the specification of the physical dimensions of all the unit processes, features of the aeration system, and particulars of the influent wastewater. This plant data can be saved to disk files which can be later retrieved.
- The STEADY-STATE menu offers steady state modeling of the unit processes. The process schematic diagram output option displays, in a tabular form, the fate of the toxic compound in the various unit processes.

This is compounded with single as well as multiple parameter sensitivity analysis for assessing the effect of varying input parameters on the removal mechanisms. The allowable influent concentrations based on specific discharge criteria can be back-calculated, as can the time-independent air emissions from the unit operations that the plant employs.

- The DYNAMIC MODELING menu of TOXCHEM is capable of handling time-variant influent flow rates and also the spillage of contaminants into the treatment plant. The results can be displayed in graphical as well as tabular format.
- The program offers a UTILITIES menu featuring useful run-time utilities like exiting to DOS, configuring the model for specific hardware requirements, and obtaining current versions as well as contact information.

As for hardware requirements, TOXCHEM can be executed on any IBM PC or compatible with 640 KB of RAM; MS DOS 3.0 or higher; hard disk with at least 1 MB reserved for the program; and an EGA, VGA, Hercules, or IBM8514 graphic adapters. Though this computer model can run without a math co-processor, the presence of one greatly enhances its execution speed.

Overview of the BASTE Model

The Baste model was not available to the authors at the time this document was prepared. The review is based on the information supplied by the company.

The BASTE model consists of a database of less than 30 compounds. Additional compounds for which the relevant physical and chemical properties are available may be added to the database. The model can analyze split flows, step feed aeration, and covered as well as uncovered processes. The model uses the following five "building blocks":

- Series of continuous flow stirred tank reactors (CFSTRs)
- Quiescent surfaces
- Weirs and drops
- Packed media
- Emission data

Each of these block types requires detailed process information such as physical dimensions, aeration rates, ventilation rates, and mixed liquor suspended solids concentration.

Experience in Running the Programs

As previously mentioned, the BASTE program was not available for review. This section describes experiences using TOXCHEM and WATER7. A comparison of features available in the reviewed models are given in Table 2.

Both of the programs come with installation modules. The user is prompted for the drive containing the installation diskette, the drive to which the program is to be installed, and the directory in which the files are to be placed. The installation module creates the required directories and copies the files to the appro-

ropriate locations.

Both the programs have a Graphical User Interface (GUI). The mouse as well as the keyboard can be utilized for selecting a menu item in the WATER7 program. The TOXCHEM program cannot use the mouse.

The menus in both the programs are clear, which makes it easy to quickly locate a menu item.

The WATER7 program prompts for missing data. For certain input parameters, default values may be used unless otherwise specified by the user. The program also flashes a warning if one of the values is perceived to be too high or too low for the case specified. This provides a safeguard against entering values outside the range normally encountered at most wastewater treatment facilities. The user can opt to continue the program with the input value.

In order to test the programs, a number of cases were run to check the software. A test case was prepared for this paper. The details of the test case are given in Table 3.

The test case was run with a single compound (dichlorobenzene 1,4) in the wastewater flow. A value of 30,000 m³/day was chosen for the flowrate. The concentration of dichlorobenzene 1.4 was assumed to be 100 µg/l with 120 mg/l total suspended solids, and 75 percent of the suspended solids were volatile. The results obtained are given in Tables 4 and 5. Table 4 contains the results from TOXCHEM and Table 5 contains the results from WATER7.

After reviewing Tables 4 and 5, one can conclude that the results obtained from both the models are in good agreement. The total air emissions reported by TOXCHEM are 455 g/day, and WATER7 reports total emissions to air to be 458 g/day (5.3E-3 grams/sec).

Conclusions

Three computer models for estimating the losses of organic compounds from wastewater treatment facilities were reviewed. No difficulties were encountered during installation and operation of the WATER7 and the TOXCHEM software. It is hoped that you will find the software useful for the preparation of emission inventories at your plant.

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Table 1. Main Menu of the Water7 Program
HELP FILE COMPOUND UNIT VIEW PRINT QUIT

```

number tagged: 0 conc.(ppmw)
  Wind velocity (cm/s at 10m)      0
  Wastewater temperature (C)       0
  Wastewater flow rate (m3/s)      0
  total dissolved organics in (mg/l) 0
  inlet solids (mg/l)              0
  Overall biorate (mg/g bio-hr)    0
  number units, pretreatment       0
  number of primary clarifiers     0
  number units equalization        0
  number of trickling filters      0
  number units aeration 1          0
  number units aeration 2          0
  number of secondary clarifiers   0
    
```

ACTIVE FILE: New file assistance not enabled

05.58:54 memory=241628 string space=6876 binary

Table 2. Comparison of Features Available in the Reviewed Models

Features	WATER7	TOXCHEM
Context sensitive help	x	x
Organics database	x	x
Modify compound properties	x	x
Upgrade database	x	x
Dynamic modeling		x
Impoundment facilities	x	
Trickling filter loss	x	
Droplet loss	x	
Storage emissions	x	
Air stream summary	x	x
DOS gateway	x	x

x = feature available

Table 3. Wastewater Treatment Plant Parameters

Wastewater flow rate (m ³ /d)		30000.00	
Wastewater temperature(°C)		20.00	
Diurnal flow pattern		NO	
Influent SS concentration (mg/L)		120.00	
Influent volatile SS fraction (%)		75.00	
Wind speed (m/s)		10.00	
Elevation of plant above sea level (m)		100.00	
Grit Chamber Characteristics		Aeration Basin(s) Characteristics	
Surface area (m ²)	100.00	Surface area (m ²)	1600.00
Depth (m)	3.00	Depth (m)	4.20
Grit chambered aerated	NO	Number of CSTR's	1
		SRT (sludge retention time) (days)	5.00
		RASSS concentration (mg/L)	3500.00
		Activated sludge recycle ratio (%)	80.00
Primary Clarifier Characteristics		Aeration system type	Diffused/Subsurface Aeration
Surface area (m ²)	1000.00	Air flow rate (m ³ /h)	6500.00
Depth (m)	3.00	Oxygen transfer efficiency (%)	12.00
Weir length (m)	140.00	Dissolved oxygen concentration (mg/L)	2.00
Weir waterfall height (m)	0.20		
SS removal in primary clarifiers (%)	50.00		
Secondary Clarifier Characteristics			
Surface area (m ²)		1650.00	
Depth (m)		4.20	
Weir length (m)		145.00	
Weir waterfall height (m)		0.20	
SS concentration in final effluent (mg/L)		10.00	
Sec. waste sludge returned to primary		NO	
Digester Characteristics			
Primary Digester Volume (m ³)		3000.00	
Primary Digester Temperature (°C)		35.00	
VSS reduction (%)		50.00	
Supernatant SS concentration (mg/L)		500.00	
Supernatant flow rate (m ³ /d)		40.00	
Sludge De-Watering Characteristics			
Final solids concentration		25.00	
Filtrate/centrate return SS (mg/L)		500.00	

Table 4. TOXCHEM Steady State Removal Summary

Location	Mechanism	Percent	Mass (g/day)
Grit chamber	Stripping	0.0000	0.0000
Grit chamber	Volatilization	0.1000	1.9900
Grit chamber	Total	0.1000	1.9900
Primary clarifier	Volatilization	1.7000	50.5000
Primary clarifier	Total	1.7000	50.5000
Aeration basin	Volatilization	0.4000	11.8000
Aeration basin	Stripping	14.6000	439.0000
Aeration basin	Biodegradation	43.9000	1320.0000
Aeration basin	Total	59.0000	1770.0000
Secondary clarifier	Volatilization	1.7000	50.6000
Secondary clarifier	Total	1.7000	50.6000
Primary digester	Stripping	0.4000	11.8000
Primary digester	Biodegradation	0.0000	0.0000
Primary digester	Total	0.4000	11.8000
Total volatilized		3.8000	115.0000
Total stripped		15.0000	451.0000
Total biodegraded		43.9000	1320.0000
Total all mechanisms/proc		62.8000	1880.0000
Total emitted to air		18.8000	455.0000
Total in wastewater liquid stream		31.9000	985.0000
Total in wastewater solids stream		5.3000	158.0000

Table 5. WATER7 Steady State Removal Summary

Source	Rate (grams/sec)	Fraction (Air)	Fraction Remaining	est. conc. (ng/m ³)
Primary Clarifier	4.644006E-03	0.1377	0.8487	0.516E+04
Aeration	5.506883E-04	0.0187	0.0188	0.551E+05
Secondary Clarifier	1.035731E-04	0.1630	0.0158	0.628E+02
All sources	5.298267E-03	0.1527	0.0158	
total fraction absorbed	1.811255E-02			

Comparison of Air Dispersion Modeling Results With Ambient Air Sampling Data: A Case Study at Tacoma Landfill, A National Priorities List Site

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Black & Veatch Waste Science Inc., 1201 Pacific Avenue, Suite 1100,
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Air dispersion modeling, ambient air sampling, and emissions testing of landfill sources have been performed to evaluate the effects of remedial activities on ambient air surrounding the Tacoma Landfill. In 1983, the Tacoma Landfill was placed on the National Priorities List (NPL) as part of the Commencement Bay/South Tacoma Channel Superfund site. Remedial activities completed, or near completion, at the 190 acre (768,903 m²) Tacoma Landfill include a groundwater extraction system and air stripping units used to remove volatile organic compounds (VOCs) from groundwater, landfill gas extraction and flare system to control gas migration from the landfill, landfill liner and leachate collection system for an active section of the landfill, and a landfill cap that covers the inactive portions of the landfill.

Dispersion modeling was performed with measured stack emission data using Industrial Source Complex (ISC) to determine the groundlevel concentrations of VOCs from the air stripper, flares, and active portion of the landfill for comparison with the measured ambient air data collected during 1992.

INTRODUCTION

Air quality dispersion modeling, ambient air sampling, and emissions testing of landfill sources were performed at Tacoma Landfill to evaluate the potential impacts of remedial activities on ambient air quality. The samples were collected as part of the landfill emissions sampling and analysis required by the U.S. Environmental Protection Agency (EPA) and the Washington Department of Ecology (collectively referred to as the agencies) to satisfy the requirements of the Tacoma Landfill Consent Decree Scope of Work. The City of Tacoma has operated the Tacoma Landfill as a solid waste disposal site since 1960. The landfill was placed on the National Priorities List of hazardous waste sites as part of the Commencement Bay/South Tacoma Channel Site as a result of an investigation conducted by the USEPA in 1983. In June 1986, the City of Tacoma began the remedial investigation and feasibility study of the site under a Response Order by Consent issued by the Washington Department of Ecology. The investigation identified the potential pathways of exposure to contamination as groundwater and landfill gas migration. The City also constructed the first stage of a landfill gas collection and flaring system in 1986. The system was expanded in 1988 and during

remedial actions performed on the site. In 1987, the City began construction of the Central Area of the landfill for solid waste disposal. The Central Area, covering approximately 33 acres (133,546 m²), was constructed in accordance with Washington State guidelines and included synthetic liners and leachate collection systems.

In March 1988, the agencies issued the Record of Decision for the site describing the selected remedial action for the site and included capping of unlined portions of the landfill; a groundwater extraction and treatment system; a landfill gas collection, flaring and monitoring system; and monitoring of groundwater, surface water, and air emissions. The City constructed a RCRA compliant landfill cap in two phases beginning in 1990 and 1991. Starting in 1992, construction of a groundwater treatment system capable of treating a flow rate of 1800 gpm (0.11 m³/s) consisting of 28 extraction wells and a treatment facility equipped with two air stripping towers. The landfill gas flaring system constructed in 1986 consisted of two Sure-lite flares. The additional gas extraction wells installed in the 1988 system upgrade and modifications made during the construction of the landfill cap resulted in additional system capacity being required. In addition to upsizing collecting piping, two new Perennial flares were installed.

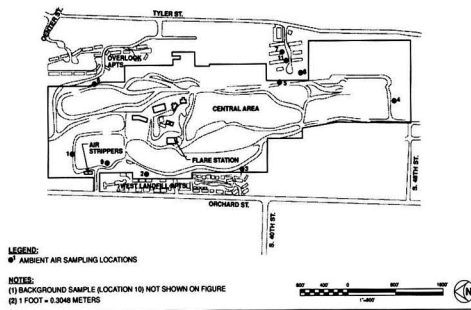


FIGURE 1. Tacoma Landfill air sample locations (October 6-7, 1992).

Remedial activities and landfill operations that potentially emit contaminants to ambient air are landfill gas flares, the groundwater treatment system air stripper, and the Central Area. Air quality dispersion modeling was performed to predict the groundlevel concentrations of contaminants resulting from the landfill sources for comparison with measured ambient air data. Sampling of ambient air coincided with emissions sampling of the landfill gas flares and an air stripper on October 6 and 7, 1992. Emissions from the Central Area were calculated using proposed guidance from the Code of Federal Regulations (CFR) [1].

This paper summarizes the results of the ambient air and emissions sampling, and air quality dispersion modeling performed to evaluate the impacts of remedial actions implemented at the Tacoma Landfill.

METHODS

Black & Veatch Waste Science Inc. (BVWS), under contract to the City of Tacoma, conducted the ambient air and emissions evaluations with the assistance of BVWS subcontractors, Coast-to-Coast Analytical Services and AmTest-Air Quality Inc.

A sampling and analysis plan that included standard operating procedures for field sampling, laboratory analysis, and quality assurance was prepared and approved by the agencies for measuring ambient air and air emissions from landfill sources, and collecting meteorological data. A description of the data collection and analysis are provided below.

Air Emissions from Landfill Remedial Activities (Landfill Flares, Groundwater Treatment Air Stripper, and Central Area)

Landfill Flares

Flare sampling was conducted on October 6 and 7, 1992. Source testing was conducted on one of the two Sure-Lite flares as well as one of the two newly constructed Perennial flares to determine the inlet landfill gas and outlet emission concentrations, mass emission rate, and the destruction efficiency of the combustion systems. The inlet gas stream of each flare was measured for temperature, velocity, flow rate, carbon dioxide, oxygen, carbon monoxide, methane, nonmethane organic carbon (NMOC), and VOCs. The emissions from each flare were measured for temperature, velocity, flow rate, moisture, carbon dioxide, oxygen, carbon monoxide, chloride (as HCl), fluoride (as HF), sulfur dioxide, nitrogen oxides, NMOC, and VOCs.

Groundwater Treatment Air Stripper

Emissions testing was conducted on the operating air stripper on October 6, 1992. Source testing of stack emissions was conducted to determine air flow rate, VOC emission rates, hydrogen sulfide emission rates, NMOC emission rates, and the composition of fixed gases. In addition, the blower inlet was sampled for VOCs and hydrogen sulfide to determine the contribution of contaminants in ambient air to emissions from the air stripper.

Central Area

Emissions from the Central Area were determined by calculation using proposed guidance listed in the federal register and measured VOC and NMOC concentrations at the landfill flare inlet [1]. The concentrations of VOCs and NMOC at the flare inlet are assumed to be representative of the gas emitted from the landfill. The gas extraction system located at the landfill was assumed to capture 60 percent of the emissions from the Central Area [2].

AMBIENT AIR SAMPLING AND ANALYSIS

Ambient air sampling was performed October 6 and 7, 1992 to evaluate the ambient groundlevel concentrations of contaminants near the Tacoma Landfill boundary. The ambient air sampling activity coincided with stack testing performed on the landfill gas flares and a groundwater treatment system air stripper.

Twelve ambient air samples at ten sample locations and one trip blank were collected during the sampling activity. Sample locations are shown on Figure 1. The locations of the sampling sites on the landfill boundaries (locations 1 through 6), which are located near the closest receptors (apartment complexes) to the landfill, were selected to provide analytical data for the sampling event regardless of the wind direction. A sample was collected in a vacant, groundlevel apartment at the east edge of the landfill (location 7). Other samples collected at the apartments were an outdoor sample (location 8) and an indoor sample at the manager's apartment (location 11). Sample location 9 represents a location near the highest expected concentrations of the combined emissions from the landfill sources (flares, air stripper, and Central Area) as determined by performing air quality dispersion modeling in preparing the sampling and analysis plan. A background sample (location 10), which is not shown in Figure 1, was located at Cheney Stadium approximately one mile to the north of the landfill.

The ambient air samples were analyzed for VOCs, NMOC, and light hydrocarbons (methane, ethane, propane, butane, pentane, and hexane). VOCs (polar and non-polar) and NMOC were analyzed using a modified EPA method TO-14 [3]. A gas chromatograph (GC) with a flame ionization detector (FID) was used to analyze methane and light hydrocarbons. A Jerome 621 hydrogen sulfide meter was used to measure the ambient concentrations of hydrogen sulfide at each sample location.

Time integrated (24 hour) ambient air samples were collected in certified clean stainless steel (SUMMA) canisters. To certify that the canisters were cleaned prior to sampling, each SUMMA canister was cleaned with humidified zero air and individually analyzed for VOCs by a modified EPA Method TO-14. No VOCs were found at, or above the practical quantitation limits following canister cleaning. Samples were collected in the evacuated SUMMA canisters by drawing ambient air through a critical orifice regulator located on each of the SUMMA canisters [3]. The critical orifice regulators were calibrated prior to, and following field sampling.

AIR QUALITY DISPERSION MODELING AND METEOROLOGICAL DATA

Air Quality Dispersion Modeling

Air quality dispersion modeling was performed using EPA model industrial source complex-short term (ISCST) to determine the predicted impacts of the landfill sources (air stripper, flares, and Central Area) on ambient air surrounding the landfill [4]. Emission rates from the landfill sources, as discussed above, were used in the air quality dispersion modeling. Air quality dispersion modeling was performed to evaluate the impact of these sources on ambient air in the vicinity of the landfill under two different cases:

- Case 1, Emissions and Conditions Measured During Testing. Groundlevel concentrations of VOCs were predicted using dispersion modeling assuming one air stripper and three flares were operating, which were the operating conditions during the stack emission testing and ambient air sampling. The predicted emissions from the Central Area, meteorological data recorded at the landfill during the ambient sampling activity, and the emission rates and source parameters measured during the stack emission testing were used in the modeling. The expected groundlevel concentrations of VOCs from each source was predicted for each location sampled in Figure 1 during the ambient sampling activity.
- Case 2, Maximum Predicted Emissions. The highest expected groundlevel concentrations of VOCs from the landfill sources during expected future operations were predicted using meteorological data recorded at Mount Tahoma High School located in Tacoma, Washington. The expected future landfill operations provided a "worse case" scenario with two air strippers and four flares operating. Predicted emissions from the Central Area were also included in the air quality dispersion modeling. The air quality dispersion modeling was performed assuming the air strippers were operating at a maximum capacity of approximately 1,800 gpm (0.11 m³/s) while treating groundwater containing "worse case" concentrations of VOCs. The expected contributions from each source on the maximum groundlevel concentrations of VOCs were also determined for this worse case condition.

The dispersion modeling was performed to provide conservative groundlevel concentrations of VOCs. The ISCST model in the urban mode was used in the dispersion modeling. The COMPLEX I model and the rural mode were not used during the air quality modeling because previous modeling activities during remedial design using ISCST and COMPLEX I in the rural and urban modes resulted in the highest groundlevel concentrations being predicted by ISCST in the urban mode. An updated version of the air dispersion model (ISCST2) is now available from the EPA [5].

Meteorological Data

Air quality dispersion modeling was performed using meteorological data measured at Mount Tahoma High School and from a station located at the landfill. A meteorological station was installed at the landfill during September 1992 in accordance with recommended guidance from the EPA [6, 7]. Meteorological data obtained from this station was used for Case 1 described above. The following meteorological data was recorded at the landfill station: wind speed (mean and instantaneous), wind direction (mean and instantaneous), standard wind deviation, air temperature at two and 10 meters, instantaneous two meter air temperature, barometric pressure, relative humidity, solar radiation, rainfall rate (millimeters per day and accumulation in millimeters), and sigma theta. Hourly

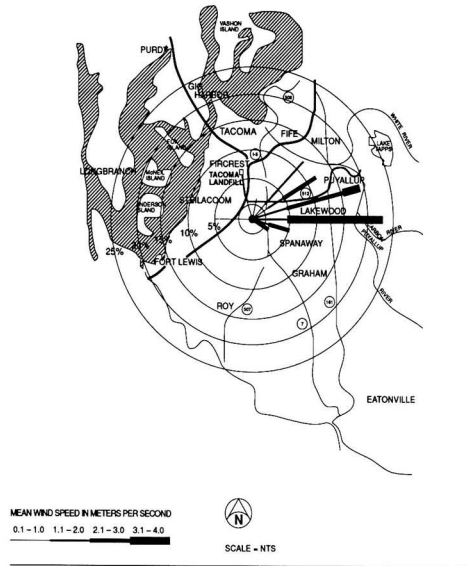


FIGURE 2. Wind rose from Tacoma Landfill meteorological station (October 6-7, 1992).

mixing heights at the landfill used in dispersion modeling for Case 1 were determined with onsite meteorological data and mixing heights from the upper air station located at Quillyute, Washington.

Five years of meteorological data are recommended for air quality dispersion modeling [8]. Since five years of on-site meteorological data were not available, data recorded at Mount Tahoma High School (located approximately 2 miles southeast of the landfill) were used for air quality dispersion modeling for Case 2. Dispersion modeling performed during remedial design of the air stripping units and the landfill gas flares with the five years of meteorological data (1978-1981, and 1987) resulted in the maximum groundlevel concentrations being pre-

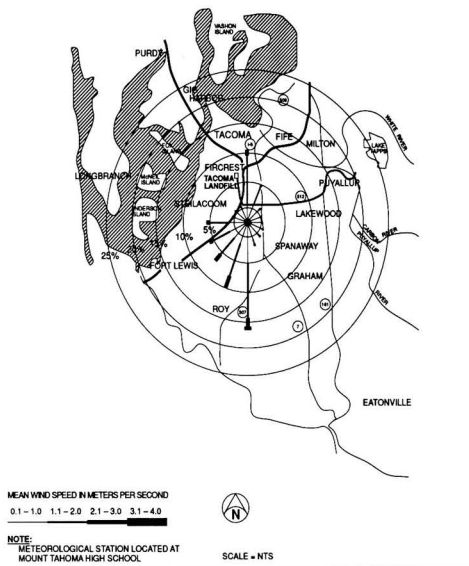


FIGURE 3. Annual wind rose for Tacoma, WA (1978-1981, 1987).

Table 1 Summary of VOCs Detected in 24-Hour Ambient Air Samples (October 1992)
(Concentrations in $\mu\text{g}/\text{m}^3$)

Compound	ASIL ^a	Sample Location											Trip Blank
		1	2	3	4	5	6	7	8	9(1)	10	11	
Acetone	5927	26	19	21	90	14	14	50	170	130	11	52	---
Benzene	(2)	3.7	6.4	3.7	3.8	4.4	5.1	7.3	5.3	5.6	3.2	6.1	--
2-Butanone (MEK)	1964	--	--	--	13	--	--	--	29	22	--	--	--
Ethylbenzene	1448	--	--	--	--	--	--	1.7	--	--	--	--	--
Toluene	1248	9.5	15	9.2	9.6	8.5	14	18	13	13	5.1	16	--
1,1,1-Trichloroethane	6327	--	2	--	--	--	--	2	--	--	--	8	--
Trichlorofluoromethane	16438	1.6	1.4	1.4	--	2.1	--	11	1.6	1.6	--	1.8	--
Trichlorotrifluoroethane	25308	--	26	--	--	9	--	--	--	29	--	--	--
Xylenes, Total	1448	4.5	5.5	3.9	3.2	3.3	6.0	11	5.6	5.2	1	3.7	--

^a Acceptable Source Impact Level from PSAPCA, Regulation III, April 1993.
(1) Maximum concentration of sample and duplicate is presented.
(2) ASIL for benzene ($0.12 \mu\text{g}/\text{m}^3$) is an annual arithmetic concentration.
-- Not detected at or above the Practical Quantitation Limit.

dicted during 1987. Therefore, dispersion modeling for Case 2 was only performed with meteorological data from 1987 to evaluate the maximum groundlevel concentrations. Figures 2 and 3 are wind roses showing wind speed and direction for air quality dispersion modeling in Case 1 and Case 2, respectively. A summary is listed below of the meteorological data for Case 1 only.

Summary of Meteorological Data Used in Air Dispersion Modeling for Case 1

Dispersion Model Hour	10 m Wind Speed (m/sec)	Stability Class Final Estimate (1), (2), (3)	Wind Direction "to" Degrees (2)	Ambient Temperature at 10 meter (K)		Mixing Heights (m)
				(1), (2)	(1), (2)	
1	3.9	C	270	286.7	1460	1460
2	2.9	C	254	287.7	1476	1476
3	3.4	C	267	288.5	1476	1476
4	3.5	C	258	289.3	1476	1476
5	3.2	C	265	289.5	1476	1476
6	2.3	C	255	288.9	1408	1408
7	2	D	236	288	1441	1441
8	1.9	D	254	286.9	1413	1413
9	2.4	D	254	286.3	1386	1386
10	2.4	D	244	285.9	1358	1358
11	1.8	E	258	285.3	235	235
12	1.3	F	233	284.9	0	0
13	1.5	F	190	284.6	0	0
14	2.2	F	295	284.9	0	0
15	1.5	F	226	284	0	0
16	1.5	F	265	284	0	0
17	1.3	F	229	283.3	0	0
18	1.5	F	272	283.3	0	0
19	1.1	F	279	283.7	61	61
20	0.9	A	201	282.9	184	184
21	0.3	A	92	282.8	307	307
22	0.9	B	74	284.1	429	429
23	0.5	A	236	285.4	552	552
24	0.7	A	229	286.5	675	675

(1) Data recorded at weather station located at Tacoma Landfill.
(2) Data used in meteorological file manually input into ISCST.
(3) Developed from On-site Meteorological Program Guidance for Regulatory Modeling Applications, EPA 450/4-87-013, P6-28.
Note: Meteorological data recorded at Tacoma Landfill during October 6-7, 1993.

RESULTS AND DISCUSSIONS

Air emissions from the landfill sources (flares, groundwater system air stripper, and Central Area) and results of the air quality dispersion modeling for Case 1 and Case 2 are described below. Ambient air monitoring results are presented with the results of the air quality dispersion modeling for Case 1.

Case 1: Emissions and Conditions Measured During Testing

Ambient Air Sample Results

Table 1 shows the analytical result summaries of VOCs and practical quantitation limits (PQLs) in the ambient air samples collected October 6 and 7, 1992. Only those VOCs that were detected at or above the PQL are listed in Table 1. Sample locations are shown on Figure 1. Samples at locations 7 and 11 were collected indoors. All other ambient air samples were collected outdoors.

Light hydrocarbons and NMOC were not detected above their respective PQLs in any of the ambient air samples. Hydrogen sulfide was detected at each sample location at concentrations less than 3 ppb ($0.12 \mu\text{g}/\text{m}^3$).

Table 1 also shows the Acceptable Source Impact Levels (ASILs) established by the local air quality control authority, Puget Sound Air Pollution Control Agency (PSAPCA), for each of the compounds detected. The ASILs are health based standards used by PSAPCA in evaluating the impacts of emission sources on ambient air quality, and for determining whether emissions control are required [9]. All of the VOCs detected in the ambient air samples are well below the ASILs. Measured 24-hour concentrations of benzene cannot be directly compared to the PSAPCA ASIL, which is an annual average concentration.

All of the VOCs, except 2-butanone and trichlorotrifluoroethane, were detected in landfill gas measured at the inlet to the gas flares during the stack emissions testing. Additionally, all of the VOCs except 1,1,1-trichloroethane and trichlorotrifluoroethane, were present in the air emissions from the air stripper. Although the ASILs are used to qualitatively assess the exposure risks associated with the ambient air samples, the VOC concentrations in Table 1 cannot be directly compared to the ASILs because sources other than the landfill may contribute to the VOCs measured at each sample location. For example, automobile emissions were probably responsible for

Table 2 Source Parameters Used in Dispersion Modeling (1)

Source	Diameter (meters)	Flow Rate (ACFM)	Temperature (K)	Height (meters)
Air Stripper	0.5207	5020	285.83	14.63
Flare	3.048	35,330	946.20	6.83

(1) Does not include Central Area. Central Area divided into 4 sections (600 feet × 600 feet, or 183 m × 183 m) with a total area of 33 acres (133,546 m²). Note: 1 ACFM (actual cubic feet per minute) = 4.7 × 10⁻⁴ m³/s (actual).

contributing acetone, benzene, toluene, and xylenes at Cheney Stadium (upwind of landfill sources) and all other sample locations. These VOCs appear to be ubiquitous in the vicinity of the landfill. Other VOCs detected (2-butanone, 1,1,1-trichloroethane, trichlorofluoromethane, and trichlorotrifluoroethane) are common solvents and used in consumer products such as canned propellants and paints, adhesives in building materials, and refrigerants.

Air Quality Dispersion Modeling

Air quality dispersion modeling was performed using ISCST in the urban mode and on-site meteorological data to determine the contribution of landfill sources on ambient air quality. Results from the dispersion modeling cannot be used for direct comparison with ambient air sample results because sources other than the landfill, as discussed above, may contribute to groundlevel concentrations of VOCs. A data summary is presented in this paper of the landfill source emissions and predicted groundlevel concentrations of VOCs using air quality dispersion modeling. Only those VOCs detected during ambient sampling (Table 1) are shown in emissions from landfill sources and for predicted groundlevel concentrations (Tables

Table 3 Emission Rates from Landfill Sources Used in Dispersion Modeling (24 Hour) for Case 1 (Emission Rates in milligrams per minute)

Compound	Flares (1),(4)	Stripper (2),(4)	Central Area (3),(4)
Acetone	22.8	64.7	15.7
Benzene	4.68	13	6.7
2-Butanone (MEK)	0.35	17.8	—
Ethylbenzene	—	11.1	99.1
Toluene	3.18	96.5	144
1,1,1-Trichloroethane	—	—	0.7
Trichlorofluoromethane	—	2.3	4.0
Trichlorotrifluoroethane	—	—	0.4
Vinyl Chloride	—	21.6	26.2
Xylenes	0.44	36	192.2

- (1) Highest average emissions rates between Sure-Lite and Perennial flares. Emissions from three flares used in determining groundlevel concentrations.
 - (2) Emissions from one air stripper used in determining groundlevel concentrations.
 - (3) Determined by calculation assuming gas collection efficiency of 60 percent.
 - (4) Additional VOCs detected during emissions testing of flares and air stripper.
- However, only the VOCs detected during ambient sampling (Table 1) are shown in this table.

— Not detected in source emissions.
 Note: 1 milligram per minute = 1.67 × 10⁻⁵ grams per second.

Table 4 Summary of Measured VOCs During Ambient Air Sampling Activity and Predicted Groundlevel Concentrations Using Dispersion Modeling (Concentrations in µg/m³)

	Location 1		Location 2		Location 3		Location 4		Location 5		Location 6	
	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)
Acetone	4.85 × 10 ⁻³	26	2.15 × 10 ⁻³	19	7.1 × 10 ⁻³	21	3.38 × 10 ⁻⁵	90	1.86 × 10 ⁻⁵	14	1.1 × 10 ⁻³	14
Benzene	9.81 × 10 ⁻⁴	3.7	4.32 × 10 ⁻⁴	6.4	2.95 × 10 ⁻³	3.7	1.21 × 10 ⁻⁵	3.8	7.73 × 10 ⁻⁶	4.4	2.22 × 10 ⁻⁴	5.1
2-Butanone (MEK)	1.01 × 10 ⁻³	—	5.8 × 10 ⁻⁴	—	9.93 × 10 ⁻⁵	—	2.63 × 10 ⁻⁶	13	2.08 × 10 ⁻⁷	—	3.03 × 10 ⁻⁴	—
Ethylbenzene	6.16 × 10 ⁻⁴	—	3.78 × 10 ⁻⁴	—	4.28 × 10 ⁻²	—	1.53 × 10 ⁻⁴	—	1.13 × 10 ⁻⁴	—	1.89 × 10 ⁻⁴	—
Toluene	5.53 × 10 ⁻³	9.5	3.17 × 10 ⁻³	15	6.25 × 10 ⁻²	9.2	2.33 × 10 ⁻⁴	9.6	1.65 × 10 ⁻⁴	8.5	1.64 × 10 ⁻³	14
1,1,1-Trichloroethane	—	—	1.21 × 10 ⁻⁷	2	3.12 × 10 ⁻⁴	—	1.10 × 10 ⁻⁶	—	8.24 × 10 ⁻⁷	—	7.23 × 10 ⁻¹⁰	—
Trichlorofluoromethane	1.25 × 10 ⁻⁴	1.6	7.42 × 10 ⁻⁵	1.4	1.74 × 10 ⁻³	1.4	6.45 × 10 ⁻⁶	—	4.59 × 10 ⁻⁶	2.1	3.85 × 10 ⁻⁴	—
Trichlorotrifluoroethane	—	—	5.93 × 10 ⁻⁸	26	1.53 × 10 ⁻⁴	—	5.40 × 10 ⁻⁷	—	4.03 × 10 ⁻⁷	9	3.54 × 10 ⁻¹⁰	—
Xylenes	2.02 × 10 ⁻³	4.5	1.2 × 10 ⁻³	5.5	8.31 × 10 ⁻²	3.9	2.98 × 10 ⁻⁴	3.2	2.19 × 10 ⁻⁴	3.3	6.13 × 10 ⁻⁴	6

- (1) Predicted using ISCST and the actual emission rates from the combined landfill sources (air stripper (1), flares (3), and Central Area).
 - (2) Measured during ambient air sampling activity (October 6-7, 1992). VOC concentrations upwind from the landfill sources have not been subtracted from the measured values.
 - Not detected above the practical quantitation limit for the measured values, or no groundlevel concentration predicted using ISCST.
- Note: 1 µg/m³ = 10⁻⁶ g/m³.

(continued on following page)

Table 4 (Continued) Summary of Measured VOCs During Ambient Air Sampling Activity and Predicted Groundlevel Concentrations Using Dispersion Modeling (Concentrations in $\mu\text{g}/\text{m}^3$)

	Location 7		Location 8		Location 9		Location 10		Location 11	
	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)	Predicted (1)	Measured (2)
Acetone	9.32×10^{-5}	50	8.62×10^{-6}	170	--	130	7.22×10^{-7}	11	6.6×10^{-5}	52
Benzene	3.95×10^{-5}	7.3	3.52×10^{-6}	5.3	--	5.6	1.45×10^{-7}	3.2	2.8×10^{-5}	6.1
2-Butanone (MEK)	--	--	1.72×10^{-7}	29	--	--	1.99×10^{-7}	--	2.97×10^{-8}	--
Ethylbenzene	5.89×10^{-4}	1.7	5.07×10^{-5}	--	--	--	1.24×10^{-7}	--	4.17×10^{-4}	--
Toluene	8.55×10^{-4}	18	7.43×10^{-5}	13	--	13	1.08×10^{-6}	5.1	6.05×10^{-4}	16
1,1,1-Trichloroethane	4.3×10^{-6}	2	3.69×10^{-7}	--	--	--	--	--	3.04×10^{-6}	--
Trichlorofluoromethane	2.38×10^{-5}	11	2.07×10^{-6}	1.6	--	1.6	2.52×10^{-8}	--	1.69×10^{-5}	1.8
Trichlorotrifluoroethane	2.11×10^{-6}	--	1.81×10^{-7}	--	--	29	--	--	1.49×10^{-6}	--
Xylenes	1.14×10^{-3}	11	9.84×10^{-5}	5.6	--	5.2	4.02×10^{-7}	1	8.09×10^{-4}	3.7

(1) Predicted using ISCST and the actual emission rates from the combined landfill sources (air stripper (1), flares (3), and Central Area).
 (2) Measured during ambient air sampling activity (October 6-7, 1992). VOC concentrations upward from the landfill sources have not been subtracted from the measured values.
 -- Not detected above the practical quantitation limit for the measured values, or no groundlevel concentration predicted using ISCST.
 Note: $1 \mu\text{g}/\text{m}^3 = 10^{-6} \text{ g}/\text{m}^3$.

Table 5 Air Emissions from Landfill Sources Used in Dispersion Modeling for Case 2 (Emissions in milligrams per minute)

Compound	Flares (1),(4)	Stripper (2),(4)	Central Area (3),(4)
Acetone	30.4	14.7	15.7
Benzene	6.24	8.67	6.7
2-Butanone (MEK)	0.46	5.31	--
Ethylbenzene	--	27.4	99.1
Toluene	4.24	29.8	144
1,1,1-Trichloroethane	--	--	0.7
Trichlorofluoromethane	--	4.52	4.0
Trichlorotrifluoroethane	--	--	0.4
Vinyl Chloride	--	16.2	26.2
Xylenes	0.59	17.5	192.2

- Four flares assumed to be operating. Highest emissions from Perennial and Sure-Lite flares (times four) used in the dispersion modeling.
 - Two air strippers assumed to be operating. Air emissions based on future expected flowrates.
 - Emissions determined by calculation. Gas extraction system assumed to remove 60% of landfill gas generated in the Central Area.
 - Additional VOCs detected during emissions testing of flares and air stripper. However, only the VOCs detected during ambient sampling (Table 1) are shown in this table.
- Not detected in source emissions.
 Note: 1 milligram per minute = 1.67×10^{-5} grams per second.

3 through 6). The following VOCs, not included in Tables 3 through 6, were detected in emissions from at least one landfill source:

Table 6 Predicted Maximum Groundlevel Concentrations From Combined Landfill Sources Using ISCST for Case 2 (Concentrations in $\mu\text{g}/\text{m}^3$)

Compound	Total Sources (24-hour)	Total Sources (annual)	ASIL
	(1),(2),(4),(5)	(1),(3),(4),(5)	
Acetone	0.07054	0.02123	5927.4*
Benzene	0.02502	0.00753	0.12**
2-Butanone (MEK)	0.00671	0.00202	1964.7*
Ethylbenzene	0.14674	0.04416	1448.6*
Toluene	0.20631	0.0621	1248.8*
1,1,1-Trichloroethane	0.00084	0.00025	6327*
Trichlorofluoromethane	0.0099	0.00298	18648*
Trichlorotrifluoroethane	0.00041	0.00012	25308*
Vinyl Chloride	0.04923	0.01482	0.023**
Xylenes	0.24409	0.07347	1488.6*

- Highest expected emissions used in dispersion modeling from two air strippers, four landfill flares, and the Central Area.
 - Predicted 24-hour ground level concentration.
 - Predicted annual average groundlevel concentration.
 - Additional VOCs detected during emissions testing of flares and air stripper. However, only the VOCs detected during ambient sampling (Table 1) are shown in this table.
 - Locations of predicted maximum groundlevel concentrations were all within the landfill boundaries.
- * ASIL based on 24-hour arithmetic mean averaging time. ASIL can only be compared to 24-hour groundlevel concentration.
 ** ASIL based on annual average arithmetic mean averaging time. ASIL can only be compared to annual average groundlevel concentration.
 Note: $1 \mu\text{g}/\text{m}^3 = 10^{-6} \text{ g}/\text{m}^3$.

- bromomethane
- bromoform
- carbon disulfide
- chlorobenzene
- chloroethane
- chloromethane
- 1,1-dichloroethane
- 1,2-dichloroethane
- dichloroethene
- cis-1,2-dichloroethene
- dichloromethane
- 4-methyl-2-pentanone
- styrene
- tetrachloroethene
- trichloroethene
- NMO

Emissions from one air stripper and three flares, which were operational during the stack testing and ambient air sampling activity, were used for the dispersion modeling. Emissions from the Central Area, estimated through calculations, were also used in the modeling. The three flares were modeled as a single point source using the operating parameters, physical dimensions, and emission rates from the Perennial and Sure-Lite flares that provided the highest groundlevel concentrations. The highest groundlevel concentrations were obtained using the lowest volumetric flow rate, highest VOC emission rates, lowest stack height, and lowest temperature from the Perennial and Sure-Lite flares. The Central Area was modeled as four area sources, each with an area of approximately 600 feet (183 m) by 600 feet (33 acres total, or 133,546 m²). Table 2 shows the source parameters from the air stripper and the flares used in the dispersion modeling.

A summary of VOC emissions from the air stripper, flares, and Central Area are shown in Table 3. Table 4 presents a summary of the VOCs detected at each sample location and the predicted 24-hour groundlevel VOC concentrations from the combined landfill sources. The predicted VOC concentrations using ISCST from the combined landfill sources ranged from two to nine orders of magnitude below the measured VOC concentrations.

Table 4 indicates that the landfill sources contribute very little to the groundlevel concentrations of VOCs at sample locations 1 through 11. The dispersion modeling using ISCST and the on-site meteorological data (24 hours) indicate that the combined landfill sources contributed groundlevel concentrations of VOCs at the ambient air sampling locations well below the PQLs. Based on this dispersion modeling scenario, the landfill sources did not contribute to the groundlevel concentrations of VOCs approaching the PQLs at the ambient air sampling locations.

Case 2: Maximum Predicted Groundlevel Concentrations

Dispersion modeling was also performed to determine the maximum 24-hour and annual average groundlevel concentrations of VOCs for future operation of the landfill sources (air strippers, flares, and Central Area). The combined and individual impacts of the landfill sources on ambient air were evaluated during dispersion modeling. Four flares and two air strippers were assumed to be operating in the dispersion modeling.

Dispersion modeling performed during remedial design of the air stripping units and the landfill gas flares with the five years of meteorological data (1978-1981, and 1987) from Mount Tahoma High School resulted in the maximum groundlevel concentrations being predicted during 1987. Therefore, dispersion modeling for Case 2 was only performed with meteorological data from 1987 to evaluate the maximum groundlevel concentrations.

A summary of air emissions from the landfill sources used in the dispersion modeling are shown in Table 5. The emissions from the Central Area and landfill flares were modeled as a single source similarly to the modeling scenario described for Case 1, except that four flares were assumed to be operating. Emissions from two air strippers were estimated based on future expected groundwater flow rates of 1,800 gpm (0.11 m³/s) and maximum predicted concentrations of VOCs.

The maximum expected groundlevel concentrations from the combined sources for annual and 24-hour averaging periods were found using the Mount Tahoma meteorological data from 1987. The locations of the maximum groundlevel concentrations from the individual, and combined landfill sources for 24-hour and annual averaging periods were all within the boundaries of the landfill. The PSAPCA ASILs and a summary of the combined source contributions to the maximum groundlevel concentrations (24-hour and annual) are shown in Table 6. All expected groundlevel VOC concentrations (24-hour and annual) for the individual and combined sources are below the respective PSAPCA ASILs. The 24-hour concentrations are several orders of magnitude lower than the respective ASILs. The groundlevel annual concentrations for vinyl chloride from the combined sources is the closest to the ASIL. The expected annual groundlevel concentration of vinyl chloride and its ASIL are 0.015 and 0.023 µg/m³, respectively.

Based on dispersion modeling results from both modeling scenarios (Cases 1 and 2), off-gas treatment is not required since the landfill emission sources (air strippers, flares, and Central Area) are not expected to produce groundlevel concentrations of VOCs that exceed the PSAPCA ASILs. Results of an analysis to evaluate Best Available Control Technology (BACT) for the air stripper and landfill flare indicated that the application of BACT could actually provide a net decrease in environmental quality. The benefit of further reducing VOC emissions from the landfill sources are off-set by the production of additional wastes and power consumption to operate BACT.

CONCLUSIONS

Air dispersion modeling, ambient air sampling, and emissions testing of landfill sources have been performed to evaluate the potential impacts of remedial activities on ambient air surrounding the Tacoma Landfill. The following results and conclusions were determined during the project:

- All of the VOCs measured in the ambient air samples are well below the PSAPCA ASIL. Off-gas treatment of landfill sources is not required.
- VOCs measured in ambient air were also detected during emissions testing at the outlet of the groundwater air stripper and at the inlet to the flares. Emissions from the Central Area were determined by calculations based on emissions testing at the flare inlet.
- Predicted contributions of groundlevel concentrations of VOCs using air quality dispersion modeling from landfill sources were two to nine orders of magnitude lower than measured values.
- Sources other than the landfill, such as automobile exhaust, probably contribute to the VOCs measured at each sample location.
- Air quality dispersion modeling predicted that groundlevel concentrations of VOCs from landfill sources should not exceed PSAPCA ASILs for current or future landfill operations.
- Air quality dispersion modeling predicted that the locations of the maximum expected concentrations from landfill sources were within the landfill boundaries.

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Using Evaporators to Achieve Zero Effluent At a BCTMP Pulp Mill

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Pulp-making is a very water-intensive enterprise, but the water recovery system at Millar Western Pulp allows the plant to use eight times less water than a conventional mill of its type (68 m³/hr makeup water vs. 568 m³/hr for the same size conventional mill) and eliminates any effluent discharge to the local river. The plant is the first pulp mill in the world to operate a successful zero liquid discharge system.

Effluent from the thermomechanical pulping process is concentrated from 2 percent solids to 35 percent solids by three falling film vapor compression evaporators, followed by two steam-driven concentrators which further concentrate the effluent to about 70 percent solids. Of the 400 m³/hr of effluent sent to the system, 391 m³/hr is recovered as high purity water for reuse in the pulping process. Solids are burned in the boiler; the smelt is cast into ingots and stored on site for future chemical recovery.

INTRODUCTION

When Millar Western Pulp (Meadow Lake) Ltd. announced plans to build a mill in northern Saskatchewan, the community was concerned about the pollution it would generate, especially effluent discharged to the Beaver River. Though a biological treatment system planned at the mill have made the effluent cleaner than river water, Millar Western decided to go one step further and eliminate all effluent discharge from the pulp mill [1].

The zero effluent system at Meadow Lake is the first of its kind in the world. It was devised by Millar Western Pulp and

the NLK Consultants, Inc., the engineers for the project. The evaporator system, the key equipment in the water recovery process, was designed and supplied by Resources Conservation Company (RCC).

All effluent coming out of the mill is treated in the water recovery plant. As a result, the mill only needs about 68 m³/hr of makeup water to replace water lost to the atmosphere by evaporation [2]. The same type of pulp mill without a water recovery plant would need about 568 m³/hr of raw water makeup.

The effluent treatment system started up in January, 1992, when the mill went on line.

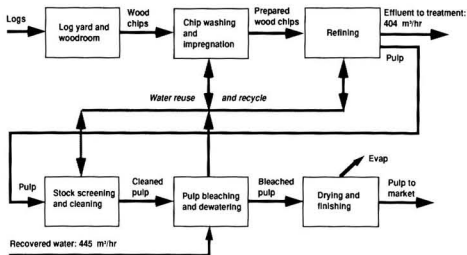


FIGURE 1. Water use in the BCTMP pulping process.

THE MEADOW LAKE MILL

The CDN \$350 million Millar Western Meadow Lake Mill is located on a 100 ha site about 320 km northwest of Saskatoon, Saskatchewan. It uses mechanical action supplemented by mild chemicals to turn aspen wood chips into bleached chemithermomechanical pulp (BCTMP), about 240,000 metric tons per year. More efficient than the kraft process, this approach uses half the trees to make the same amount of pulp, producing almost one ton of pulp for each ton of wood on a water-free basis. The Millar Western BCTMP process also eliminates chlorine compounds and odorous sulfur-based impregnation chemicals. This environmentally-friendly mill uses hydrogen peroxide to increase the brightness of the pulp, making it suitable for printing and writing grades of paper as well as for tissue and paper towels.

Figure 1 shows the BCTMP pulping process and its use of recovered water.

THE ZERO EFFLUENT WATER RECOVERY SYSTEM

The effluent produced by the BCTMP process is discharged at a rate of about 409 m³/hr. It has a temperature of 66°C, a pH of about 8 and contains about 20,000 ppm dissolved solids. Figure 2 shows the overall water treatment process including softening of the raw water makeup. Figure 3 shows a more detailed view of the water recovery portion of the system, consisting of five stages: clarification, evaporation, concentration, stripping, and incineration.

Clarification

The first unit operation to receive pulp mill wastewater is the floatation clarifiers. Since removal of fiber is very important to the performance of the evaporators, the mill decided

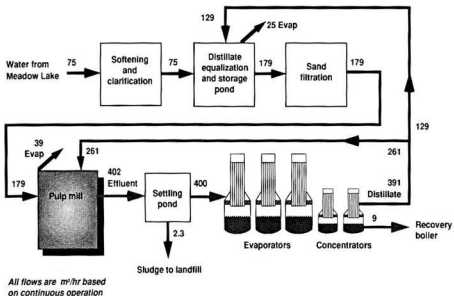


FIGURE 2. Millar Western water recovery process overview.

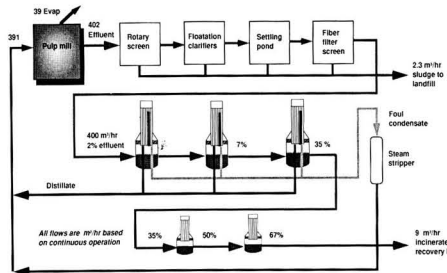


FIGURE 3. Millar Western effluent treatment system.

to install two clarifiers instead of one. This allows for maximum removal efficiency and flexibility. Chemicals are added to aid in flocculation and floatation of the solids.

To ensure that upsets in the pulp mill do not directly affect the evaporators, an on-line meter measures suspended solids in the clarifier accepts stream. When the suspended solids exceeds 900 ppm, the clarifier accepts are directed to the settling ponds. Clarifier accepts normally go directly to the evaporators in the winter to conserve heat. In the summer the accepts go preferentially to the settling pond to dump heat since the heat balance changes from season to season.

Evaporation

The heart of the zero effluent system is three vertical-tube, falling-film vapor compression evaporators. At 30 m tall, and with thousands of square meters of heat transfer surface, this is the largest train of mechanical vapor recompression evaporators in the world. The evaporators concentrate effluent from 2 percent to 35 percent solids, using an energy-efficient mechanical vapor-compression process to recover distilled water from the effluent. The evaporator consists principally of a heating element, vapor body, recirculation pump, and a vapor compressor (Figure 4).

The effluent is pumped from the vapor body sump to the top of the heating element (tube bundle). A distributor is installed in the top of each tube, causing the effluent to flow down the inside of each tube in a thin film. The distributor helps prevent fouling of the heat transfer tubes by keeping them evenly and constantly wet. It also allows the mill to operate at reduced capacity if desired, since the heating surfaces will remain wet regardless of the amount of effluent being processed. (The evaporators are also capable of handling 1.2 times more than design flow rates from the pulp mill which

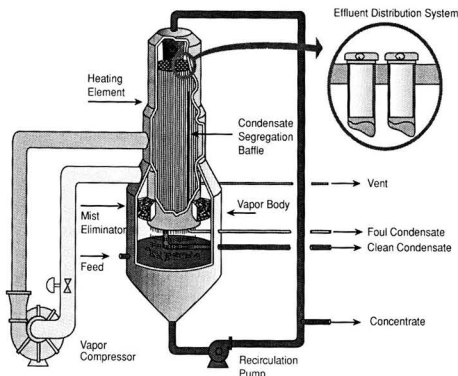


FIGURE 4. Evaporator.

gives the mill a significant amount of catch-up ability.) When the effluent reaches the bottom of the tubes, the recirculation pump sends it back to the top for further evaporation.

As the effluent flows through the heated tubes, a small portion evaporates. The vapor flows down with the liquid. When it reaches the bottom of the tube bundle, the vapor flows out of the vapor body through a mist eliminator and then to the compressor, which compresses it a few psi. The compressed steam is then ducted to the shell side of the tube bundle, where it condenses on the outside of the tubes. As it does so, it gives up heat to the tubes, resulting in further evaporation of the liquid inside. A large amount of heat transfer surface is provided, which minimizes the amount of energy consumed in the evaporation process. Operation of the vapor compression evaporator system requires only 17 kWh per m³ of feed.

As the vapor loses heat to the tubes, it condenses into distilled water, which flows down the outside of the tubes. Because the water that first condenses out of the steam is cleaner than water condensing later, baffles are provided within the heating element to create two separate regions for condensing. Steam flows first through the clean condensate region where most condenses. The remaining vapor, which is rich in volatile organics such as methanol, condenses in the foul condensate region of the heating element.

A major portion (70 percent) of the clean condensate is sent directly to the pulp mill for use as hot wash water at the back end of the mill. The balance of the clean condensate goes to the distillate equalization pond where it is combined with makeup water from Meadow Lake and serves as the cold water supply to the mill. The foul condensate, which contains the volatile organic materials, is reused after stripping in a steam stripper.

Virtually nothing more than a minor vibration problem in the evaporator electrical motors was encountered during the startup, allowing continuous operation with no unscheduled down time to affect pulp mill production.

Concentration

Like the three evaporators, the two concentrators are vertical-tube, falling-film design. Rather than using a vapor compressor to drive the system, the concentrator is operated with steam generated by the recovery boiler.

The evaporation process in the concentrators is essentially the same as in the evaporators, but the effluent is concentrated further, to about 67 percent solids. The concentrated effluent is incinerated in the recovery boiler. The lead concentrator takes the liquor from 35 percent to 50 percent, while the lag concentrator goes from 50 percent to 67 percent solids.

During startup, there was some concern that the final liquor might be too thick to pump. As it turned out, the liquor was easy to handle at operating temperatures. Since startup, no serious plugging has occurred in the concentrators and scaling has been minimal. Each concentrator can be switched to water wash mode while liquor storage tanks are drawn down, then placed back in service with no shutdowns upstream at the evaporators or downstream at the recovery boiler.

Stripping

The foul condensate, only about 10 percent of the total condensate, is stripped of volatile organics in a packed column stripper. Volatile organics are selectively concentrated in the foul condensate because of the condensate segregation features built into the evaporator heating elements. Process steam from the concentrator is sent to a reboiler, which generates stripping steam from a portion of the stripped condensate. The stripped condensate is combined with the clean condensate and reused

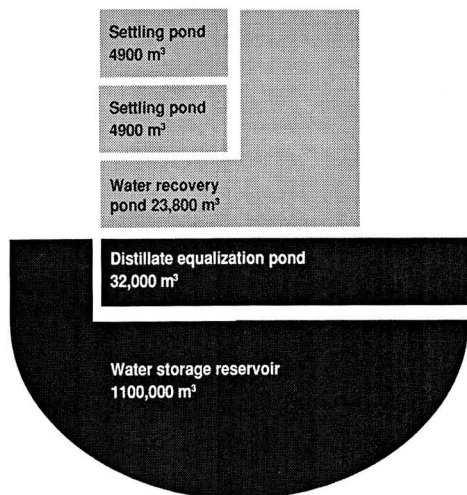


FIGURE 5. Millar Western water ponds.

in the mill. The stripped volatile organics are incinerated in the recovery boiler as a concentrated vapor.

Incinerator

At the recovery boiler, the organic components of the effluent are incinerated, a process that also generates steam to operate the concentrators. Inorganic chemicals in the effluent are recovered in the smelt from the boiler, which is cast into ingots and stored on site. The mill is considering recovering the sodium carbonate, which would then be converted to sodium hydroxide, a major chemical used in the BCTMP process.

WATER STORAGE

In the mill there are many tanks and chests for storing white water, pressates, and wastewaters. Likewise, in the water recovery plant there are storage chests for mill water and various concentrations of liquor. But the heart of the water storage system lies in five major ponds holding 182,000 m³ (Figure 5). The ponds are split into two settling ponds and one water recovery pond holding all wastewater volumes. The two settling ponds hold 4900 m³ each and are concrete-lined to facilitate dredging when required. The water recovery pond holds 23,800 m³ of wastewater and is concrete-lined along the sides to prevent erosion and clay-lined on the bottom.

The distillate equalization pond and water storage reservoir hold all the clean water. The distillate equalization pond is a bio-polishing pond where the small amount of volatile organics that come over with the distillate are consumed by biological action. This pond holds 32,000 m³ while the water storage reservoir holds 110,000 m³. Both ponds have a 1.5 mm poly liner.

Having the large storage basins for wastewater give the pulp mill two days of run time with the water plant completely shut down. If makeup water from the lake is down, the pulp mill can run for 20 days from clean water inventory in the water storage reservoir. Also, if there is a recovery boiler outage, the pump mill and evaporators can continue to run for 30 days without being affected.

Without the pond system, the operation of the pulp mill would be totally dependent on the operation of the water

recovery plant. An evaporator trip or recovery boiler outage would directly cause lost production in the pulp mill. Because the design is so flexible, an evaporator trip has no effect whatsoever on pulp mill production. An emergency shutdown in the pulp mill allows for slow turndowns in the water plant.

CONCLUSION

Perhaps the best way to describe the success of the water recovery plant is that the pulp mill operators barely recognize that they are in a zero effluent environment. They have access to all the water they require and it is better quality than lake or river water. The water recovery plant has not caused any lost production in the pulp mill other than for normal maintenance of the equipment. No off-grade pulp has been produced as a result of water quality. Washing efficiencies have been excellent and the cleanliness of the pulp, not only in terms

of debris, but also organic loading, has been better than expected [3]. In short, the zero effluent mill has proved to be a success.

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Biofilter Treatment of Ethanol Vapors

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Bench scale experiments and a numerical model were used to test the effectiveness of biofiltration in treating air contaminated with ethanol vapors. Three packing materials, granular activated carbon, compost, and a mixture of compost and diatomaceous earth were tested. The GAC material supported the highest elimination rates, ranging from 53 to 219 grams/m³-hr for a range of loading rates. Partitioning coefficients for the contaminant on the biofilter packing material had a strong effect on the efficiency of the biofilters.

INTRODUCTION

Recently, ethanol emissions have become subject to regulatory control. In California, the South Coast Air Quality Management District requires volatile organic compound (VOC) emissions to be under 600 lbs per day for stationary sources and has adopted a regulation (Rule 1153) that requires commercial bakeries to control ethanol emissions. Biofiltration offers a cost-effective treatment for certain waste-gas streams when compared to other Air Pollution Control (APC) options [1]. This work investigates the applicability of biofilters to treatment of air contaminated with ethanol vapors.

Biofiltration is a relatively new control technology that utilizes microorganisms in the aerobic destruction of pollutants. Waste gases are purified by passage through a biologically active porous medium. As the air moves through the biofilter, contaminants pass into a wet biofilm layer surrounding the support particles and are degraded to carbon dioxide and water, or incorporated into biomass.

Traditional approaches to biofilter treatment have focused on compost as the filter medium [2, 3, 4]. Most operating systems in Europe use compost. It is cheap, with a large existing microbial population capable of degrading various pollutants. Buffer capacity is adequate and inorganic nutrients are available. However, compost is prone to aging phenomena, including compaction and lumping of material that decrease effectiveness of the biofilter. Other materials have characteristics that may promote higher elimination capacities for a given volume of material, providing possible economic advantages [5, 6].

Bench-scale batch and continuous flow experiments were done to evaluate biofiltration in the treatment of waste-gas streams contaminated with ethanol. The efficiency of three different packing materials: granular activated carbon (GAC), compost, and a mixture of compost and diatomaceous earth

(compost/D.E.), was compared for different operating conditions. A mathematical model was developed that describes basic transport and biological processes and model predictions were compared with the experimental results.

THEORETICAL BACKGROUND

Analyses of the processes of a biofilter have been described by Ottengraf [2, 3], Devinny et al. [7], and Hodge et al. [5]. In order to represent processes for steady-state and nonsteady-state conditions, numerical solutions to one-dimensional differential equations were developed. A two-step explicit finite difference approximation technique was effective in solving the differential equations. Given initial and boundary conditions, the model predicts contaminant, carbon dioxide and hydrogen ion concentration profiles.

The model describes transport and biological processes as a function of distance through the column. The biofilter is treated as a two phase system, with one equation describing concentrations in the air, and a second equation describing concentrations in the solids and water (solids/water). Contaminant concentration in the air is controlled by advection, dispersion, and transfer to the solids/water phase. Transfer is assumed to occur instantaneously, establishing a constant concentration ratio between the solids/water and the air (the partition coefficient). Within the solids/water phase, contaminant concentration is increased by transfer from the air phase and decreased by biodegradation. Biodegradation is assumed to occur at a rate proportional to the contaminant concentration (first-order kinetics). Treating the solids and water as a single phase ignores important phenomena, such as diffusion in the water/biofilm layer and details of the adsorption processes at the water-solid interface. However, the simplification is acceptable for modeling heterogeneous filter materials.

The model also describes the evolution of carbon dioxide by the microorganisms and predicts concentration profiles in the filter by the same basic processes used for the contaminant concentration. Buffering capacity values for the specific media are used along with carbon dioxide concentrations to evaluate H^+ concentrations.

The model was used in this study to predict substrate and carbon dioxide concentration profiles for both the air and solids/water phases and H^+ concentration profiles for the solids/water phase of the biofilter. Both steady-state and non-steady state conditions are described.

MATERIALS AND METHODS

Packing Materials

Granular Activated Carbon

The GAC was manufactured by Calgon (1 mm granules, for water treatment). The material was inoculated with 1 percent by weight seed soil from a petroleum refinery landfarm. Nutrient concentrations were supplemented by the addition of 20 mg of $(NH_4)NO_3$ and 6 mg of K_2HPO_4 per 100 grams material.

Sintered Diatomaceous Earth

The diatomaceous earth was manufactured by the Manville Company (1 mm granules). The material was inoculated with 1 percent by weight seed soil from a petroleum refinery landfarm. Nutrient concentrations were supplemented by the addition of 20 mg of $(NH_4)NO_3$ and 6 mg of K_2HPO_4 per 100 grams material.

Compost

The compost material was yard waste (grass clippings, tree material, etc.) that was composted for approximately three months before use. Moisture content in all three materials was brought to field capacity by adding distilled water.

Methods

Gas Concentration Determination

An SRI model 8610 gas chromatograph, equipped with a flame ionization detector (FID) and interfaced with a Hyundai 386 computer with SRI's Peaksimple II data system/integrator, was used for analysis of gas concentrations. A bypass chromatograph column was used for most analyses. It consisted of a stainless steel tube 10 cm long \times 1 mm i.d. with no internal packing material. Response from the FID detector was immediate after sample injection, allowing for a large number of analyses in a short period of time. The carrier gas had a 10:1 ratio of air to hydrogen at flow rates ranging from 5 to 10 ml/min.

Carbon dioxide concentrations were also determined with the gas chromatograph. A capillary column separated carbon dioxide from other constituents in the gas samples. Because the FID cannot detect CO_2 directly, a methanizer was attached in-line after the capillary column and before the FID. With hydrogen supplied as the carrier gas, CO_2 is catalytically reduced to methane by passage through the methanizer. The methanizer column consisted of a 7.5 cm long \times 3.2 mm i.d. stainless steel tube filled with a special nickel powder which was heated to 375°C. The CO_2 is detectable by the FID to 1 ppm with this system.

Partition Coefficient Studies

Partition coefficients, k_h , were estimated by flask experiments. Sealed, 25 cc flasks with septum-covered screw-on caps held approximately 10 cc of biofilter material. Both flasks and material were autoclaved before addition of known amounts of ethanol. Flasks were kept in a constant temperature incubator. Headspace samples were taken until equilibrium was reached between the air and solids/water phases. The value of k_h was determined by the following relationship:

$$k_h = \frac{C_{ads}}{C_{air}} = \frac{(\text{contaminant added, mg}) - (\text{contaminant in air phase, mg})}{\text{Volume of solid/water phase, cc} \times \text{concentration in air phase, mg/cc}} \quad (1)$$

where

C_{ads} = contaminant concentration in the solids/water phase, mg/cc;

C_{air} = contaminant concentration in the air phase, mg/cc.

The ratio of the masses of contaminant in the two phases (k_m) is:

$$k_m = \frac{M_{ads}}{M_{air}} = \frac{C_{ads}(1-\theta)}{C_{air}\theta} = k_h \left(\frac{1-\theta}{\theta} \right) \quad (2)$$

where,

M_{ads} = mass of contaminant in the solids/water phase, mg;

M_{air} = mass of contaminant in the air phase, mg;

θ = filter material porosity at field capacity; unitless.

Carbon Dioxide Evolution Rate Studies

The procedure for respiration determination (CO_2 evolution rate) utilized sealed, 25 cc flasks with septum covered screw-on caps which held approximately 10 cc of biofilter material. The objective of the study was to determine the respiration rate of the biofilter material under different conditions. Flasks were autoclaved before filter material was added. After filter material was added, flasks were incubated at 20°C for 24 hours. The concentration of CO_2 in the head space of the flasks was measured before and after incubation. The difference in those two concentrations was used to calculate the CO_2 evolution rate. Results are expressed as grams of CO_2 evolved per gram biofilter material per hour.

Continuous Flow Column Studies

The bench scale column apparatus consisted of polyvinyl chloride plastic (PVC) columns with an inner diameter of 7.6 cm and height of 90.0 cm (Figure 1). Columns were sealed at each end with PVC caps fitted with hose barbs for influent and effluent flows. Sampling ports consisted of holes drilled in the PVC and covered by rubber septa. Peristaltic pumps supplied air flow to the columns. One air stream passed through water to provide humidity while another passed through ethanol. Flows were independently measured by flowmeters. Backpressures were determined by a water manometer before the combined flow entered the column.

Air samples were taken with disposable syringes (5 cc in volume). Three 0.25 cc samples were taken per sampling port

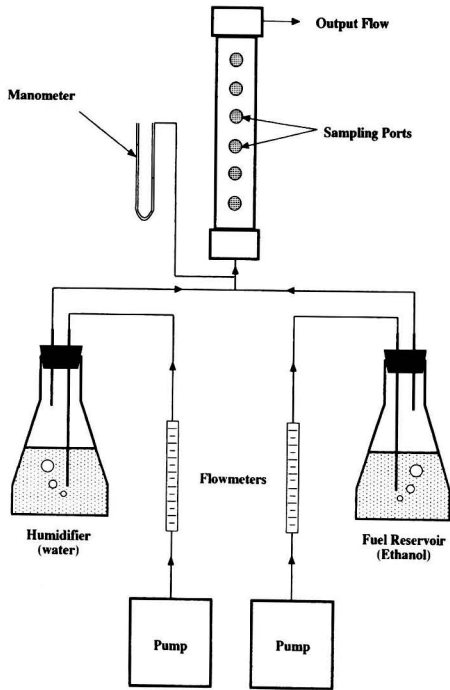


FIGURE 1. Schematic of experimental continuous flow apparatus.

and injected into the GC. The average concentration of the three injections was used for data analysis. After each sample collection, the syringe was cleaned with syringe cleaner (Hamilton Company, Model 76610).

Biofilter Elimination Rate Determination

Elimination rates for the biofilters were determined using the relationship between the influent and effluent air phase concentrations, air flowrate, and the volume of biofilter material. Rates were expressed as mass of contaminant degraded per volume of filter material per time and were calculated from the following equation:

$$E_R = (C_{inf} - C_{eff}) \times Q / \text{Volume} \quad (3)$$

where,

E_R = elimination rate, g/m³/hr;

Q = flowrate, m³/hr;

C_{inf} = influent air phase contaminant concentration, g/m³;

C_{eff} = effluent air phase contaminant concentration, g/m³; and

Volume = volume of biofilter packing material, m³.

Microbial Degradation Rate Studies

Steady-state conditions were achieved in the biofilter columns for several loading rates. During these periods, biological degradation rates were determined by a least-squares fit for the concentration gradient profiles. Equation (4) was used,

with values for contaminant partitioning (k_m), surface loading rate, and porosity for determination of biological degradation rate constants (b). Derivation of equation (4) has been described [5]:

$$C = C_0 \exp\left\{-\frac{bk_mx}{V}\right\} \quad (4)$$

where

C = constituent concentration in air phase, mg/cc;

C_0 = initial substrate (contaminant) air phase concentration, mg/cc;

b = first-order biological rate constant, per hour;

x = distance of penetration in filter, cm;

V = axial interstitial velocity in air phase, cm/hr.

Retardation Factor Studies

The retardation factors (R) for the contaminants on the biofilter material were estimated using a pulse experiment. A stable concentration gradient was first established in the column. Then the influent concentration was doubled for a period of time (usually 24 hours) and then returned to initial value. A spike (pulse) of contaminant was produced in the concentration gradient and was followed through the column by sampling periodically. The average peak velocity was evaluated by comparing two profiles taken at different times and measuring how far the peak had moved. The retardation factor (R) was determined by dividing the interstitial velocity by the peak velocity. Values of k_m and k_h were then calculated from equations (2) and (5):

$$R = \frac{M_{ads} + M_{air}}{M_{air}} = 1 + k_m \quad (5)$$

Carbon Dioxide Evolution Rate Studies

Concentration profiles for CO₂ were measured by sampling at various depths. Quantitative analysis of the concentrations helped validate microbial activity, estimated equilibrium conditions, and indicated microbial kinetics for the mineralization of the substrate.

RESULTS

The results included experimental and numerical model analysis of biofiltration in the treatment of vapor contaminated with ethanol. The efficiencies of compost, granular activated carbon, and a mixture of compost and diatomaceous earth (50 percent each, by volume) as biofilter media were evaluated.

Partition Coefficient Studies

Partition coefficient values were estimated by batch (flask) experiments. Sealed flasks containing autoclaved GAC samples were spiked with known amounts of ethanol. Headspace samples were taken until equilibrium was reached. Concentrations of ethanol in the solids/water phase were correlated with concentrations in the air phase for compost, compost/D.E., clean GAC (new GAC) and GAC with biofilm (used GAC) to estimate k_p values (Figure 2). The clean GAC had much higher values of k_p than the other samples (Table 1).

Values for partition coefficients were also estimated with continuous flow pulse experiments. Approach velocities were

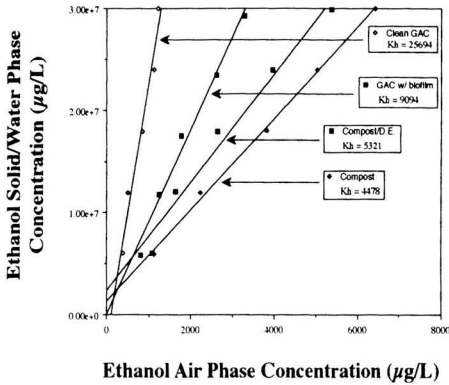


FIGURE 2. Flask experimental results for ethanol partitioning for the different biofilter media.

Table 1 Biofilter Packing Material Characterization

	Batch Experiments			
	Compost	Comp/D.E.	GAC	Clean GAC
Partition Coef, k_h	4480	5320	9090	25700
Retardation Factor	5500	6500	27300	77100
Porosity, %	45	45	25	25
	Continuous Flow Experiments			
	Compost	Comp/D.E.	GAC	Clean GAC
Partition Coef, k_h	2900	4400	8700	—
Retardation Factor	3600	5400	26000	—
Biodegradation Rate	0.0061	0.0055	0.0032	—
Constant, b (per hr)				
bk_m	22	30	83	—

held constant at 23.7 m³/m²-hr. The average peak velocity for the GAC, compost/D.E. and compost media was 0.36, 0.96 and 1.45 cm/hr, respectively. Values for R , k_m , and k_h were determined for each biofilter. The GAC had relatively high values compared to the other media (Table 1).

Degradation Rates

Studies were conducted to compare model predictions and experimental data for three steady-state loading conditions (Figures 3, 4, and 5). Three pollutant concentration profiles, with respective load and elimination rate values, were prepared. The loading rates were varied by changing the influent concentration while keeping the flowrate the same. The biological degradation rate constant (b) was calculated for each profile using equation (4), and the average of these values (for each biofilter medium) was used for all the model simulations presented. The rate constants (b) for compost, Compost/D.E., and GAC were 0.0061, 0.0055, and 0.0032 per hour, respectively. First-order biological rate constants correlated better with experimental data than zero-order rate constants.

The model predictions were in agreement with experimental data for the two lower loading conditions. Effluent concentrations were accurately predicted. The shapes of the concentration gradient profiles differed slightly. For the high-load experiment, possible channeling effects caused variability.

The elimination rates for each profile in Figures 3–5 were calculated. Rates strongly correlated with load for the three biofilter media during steady-state operations (Figure 6). As biofilter load was increased, the elimination rate for the biofilters increased. The experimental data for the GAC, compost/

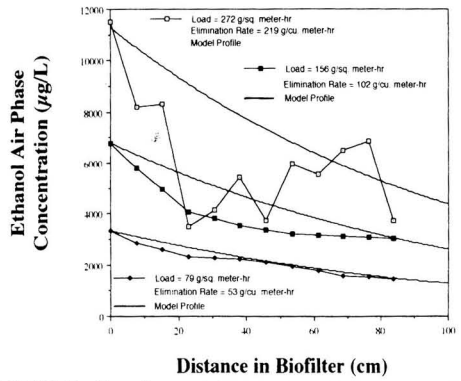


FIGURE 3. Experimental data and model predictions for the GAC biofilter for three different loading conditions.

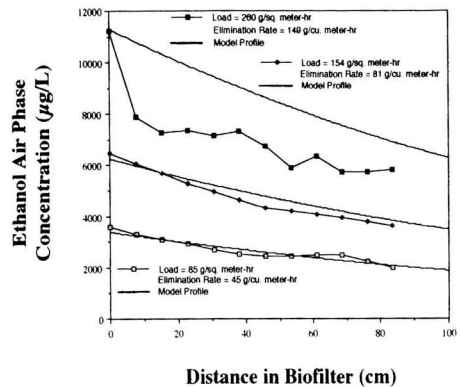


FIGURE 4. Experimental data and model predictions for the compost/diatomaceous earth biofilter for three different loading conditions.

D.E., and compost biofilters have correlation coefficients (R) of 0.96, 0.97, 0.91, respectively. Results show the dependence of elimination rate on contaminant load, suggesting first-order degradation kinetics. The GAC biofilter showed the highest elimination rates for the range of contaminant load tested.

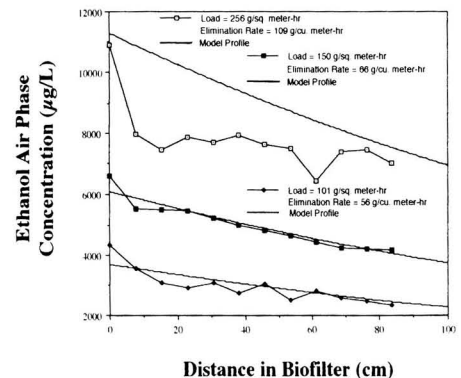


FIGURE 5. Experimental data and model predictions for the compost filter for three different loading conditions.

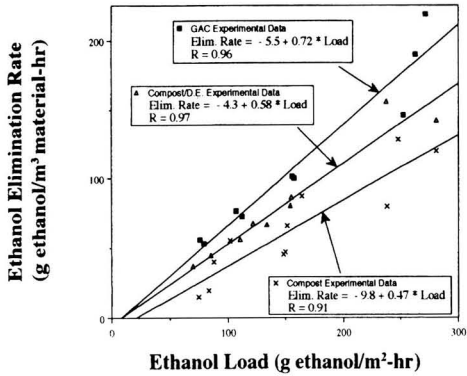


FIGURE 6. Experimental data comparing elimination rates of the three biofilters for a range of contaminant loads with approach velocity held constant.

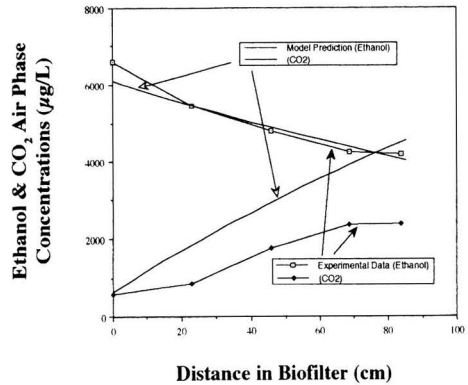


FIGURE 9. Experimental data and model predictions for ethanol and CO₂ concentration profiles for the compost biofilter.

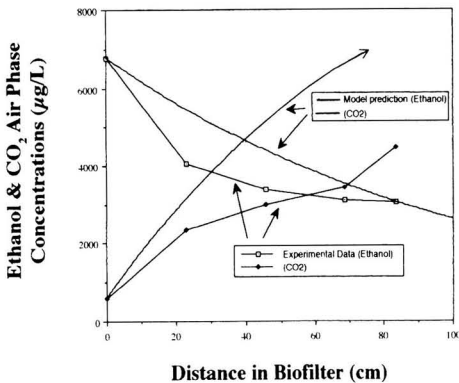


FIGURE 7. Experimental data and model predictions for ethanol and CO₂ concentration profiles for the GAC biofilter.

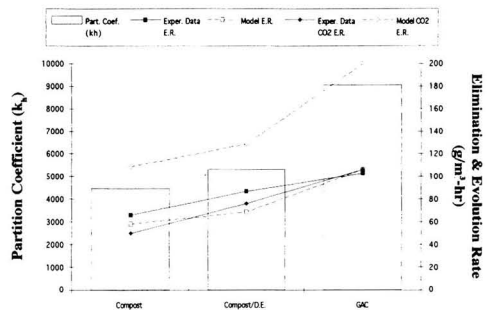


FIGURE 10. Experimental results and model predictions for ethanol elimination rates and CO₂ evolution rates. Ethanol loading rates held constant.

Carbon Dioxide Evolution Rate Studies

Both model predictions and experimental data for ethanol and carbon dioxide concentration gradient profiles at steady-state conditions were developed (Figures 7, 8, and 9). As ethanol concentrations decreased, carbon dioxide concentrations increased through the length of the biofilters.

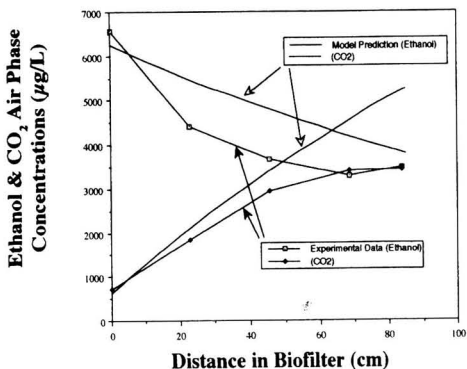


FIGURE 8. Experimental data and model predictions for ethanol and CO₂ concentration profiles for the compost/diatomaceous earth biofilter.

Elimination rates, CO₂ evolution rates, and partition coefficient values (k_a) were compared for the steady-state conditions presented in Figures 7–10. Both experimental data and model predictions show that the GAC biofilter had the highest elimination rate and CO₂ evolution rate for similar loading conditions. Values determined for the CO₂ evolution rate by the model were approximately double those calculated from the experimental data. One explanation is that there is not complete mineralization of the substrate and that a portion is being incorporated into biomass.

Batch tests designed to test the respiration rate of the packing material also indicated that GAC had the highest CO₂ evolution rate (Figure 11). Two samples were taken per biofilter, one from near the inlet and one from near the outlet and the average of the two sample results was used for the comparison. Flasks were sampled and aerated four times during the testing period. For three of the four sampling periods, the GAC biofilter media produced the most CO₂ followed by compost/D.E. and then the compost media.

The accumulation of CO₂ in the solids/water phase could lower the pH in the biofilters. Model simulations predicted that for a GAC biofilter the pH at the entrance and exit of the filter material would be 7.0 and 6.0 respectively for loading conditions tested in the lab. Experimental data values were 4.8 and 4.2, respectively. Both model predictions and experimental results for the compost and compost/D.E. biofilters showed no pH reduction. Alkalinity and carbonate concentrations for these biofilters are significantly higher than for the GAC biofilter, providing sufficient buffer capacity.

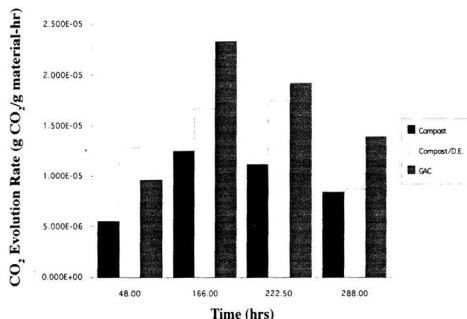


FIGURE 11. Batch (flask) test averaged results for CO₂ evolution rates of media taken from the biofilters.

Backpressure Analysis

The relation between backpressure and surface loading rate is an important parameter for energy consumption determinations [8]. The effect of surface loading rate on pressure drop across the three biofilters was tested (Figure 12). Two sets of experiments were carried out. The first set characterized the "new" biofilter material at field capacity moisture content levels before substrate addition. The second set evaluated the pressure drops for the "used" biofilter material after three months of continuous operation. As expected, the pressure drop increased as the air flow was increased for all the biofilters. The compost/D.E. biofilter showed the smallest pressure drops. There was a significant increase in backpressure for the "used" GAC, possibly because of biomass accumulation.

CONCLUSIONS

The mathematical model used in this study assumed that biodegradation followed first-order kinetics. Experimental data and numerical model predictions agreed well. Results suggested that the elimination rate was dependent on the filter's contaminant load for the range of values tested.

The numerical model was a valuable tool for biofilter performance evaluation. It successfully separated the effects of adsorption from biodegradation, determined the time needed

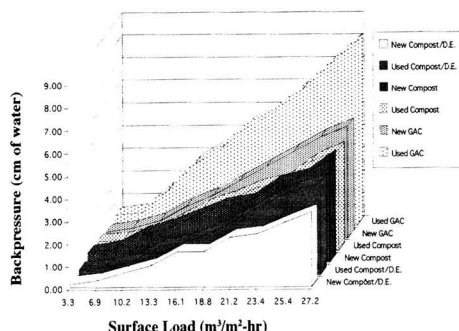


FIGURE 12. Backpressure vs. surface load profiles for new and used biofilter material.

to reach steady-state conditions, and approximated carbon dioxide concentrations from microbial degradation.

Quantitative analysis of carbon dioxide concentrations in biofilters validated microbial activity, helped determine steady-state conditions, and indicated microbial kinetics. At steady-state conditions, the model predicts ethanol concentration decreases and carbon dioxide concentration increases through the length of the filter (Figures 7-9). Experimental data substantiates this pattern, although carbon dioxide concentrations are lower than predicted values. One explanation for the difference is that a portion of the contaminant is used for cell mass production. The model assumes that all oxidized contaminants are converted to CO₂ and water.

Results show that the ratio of concentration of contaminant between the solids/water and air phases at equilibrium (partition coefficient, k_h) is an important filter media design parameter. Two different techniques were used to measure the partition coefficients with reasonable agreement between the two. The differences may have resulted from difficulties in controlling the water content in the column experiments. Results from other studies suggest that the water content affects the adsorptive properties of the filter material. For certain filter materials the adsorptive capacity increases with increases in the moisture content. This is the case with ethanol because of its hydrophilic nature. The water phase accounts for the majority of adsorptive capacity of the filter material [5].

For the three biofilter materials tested, there was a strong relationship between partitioning values, ethanol elimination rates, and CO₂ evolution rates (Figure 10). GAC had the highest partition coefficient values, elimination rates, and CO₂ evolution rates. First-order degradation kinetics predict that filter media with the greatest adsorptive properties (k_h values) will have the highest filter elimination rates if the adsorbed contaminant is biodegradable.

Compost supported the highest degradation rate (b) (Table 1). GAC had the lowest. This suggests that compost material offers a better environment for microbial growth and activity. The structure of a GAC particle allows biological growth only on the surface and in pores sufficiently large for microbial cells. Therefore, a large portion of a GAC particle does not support growth. However, the bk_m values for the GAC material were still higher than for the compost (Table 1). For GAC, the value for bk_m (equation 4), determined from continuous flow experiments, was 83 per hour compared to a 22 per hour for the compost. The higher value of b for compost is overwhelmed by the higher value of k_h for GAC, accounting for the higher overall elimination rates and bk_m values for GAC.

While GAC supported higher rates of treatment, other factors must be considered in the choice of treatment medium. GAC is substantially more costly, and for any particular application it must be determined whether the benefits of reduced biofilter size are sufficient to justify its use. Biofilm growth substantially reduced k_h values for GAC (Figure 2), although they remained relatively high. No long term experiments (years) have been reported, but it seems likely that GAC will be less susceptible to the medium compaction which is a problem for compost biofilters. Increases in filter backpressure values and channeling effects on GAC were probably due to biofilm growth. Percent ash tests also showed increases in organic matter on the GAC particles with time, substantiating buildup of biomass. Larger size GAC particles could mitigate these problems.

Both experimental and model results showed a decrease in the GAC biofilter material pH because of oxidation of the contaminant. The model described effects of carbon dioxide concentration on pH. The differences in experimental and model values suggest accumulation of additional by-products (e.g., organic acids). For filter material with low buffer capacity and carbonate concentrations, chemical buffers, such as lime and soda ash, should be added.

Measured treatment rates for the three media tested were high in comparison to other results for biofilters [3, 9, 10].

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A Batch Reactor for Monitoring Process Dynamics During Biodegradation Of Volatile Organics

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Data are presented that demonstrate a batch reactor that allows accurate monitoring of process dynamics during biodegradation of volatile organics. Using this system, many samples can be removed in a aseptic fashion, allowing frequent measurements of the concentrations of biomass, electron donors, electron acceptors, and volatile compounds. Additionally, the reactor is well instrumented, allowing the continuous monitoring of pH, oxidation/reduction potential, pressure, and temperature. The reactor is constructed entirely of materials which have minimal interaction with volatile organic compounds. It is also demonstrated that sample removal does not cause losses of volatile compounds since the sampling ports are double sealed, making use of both gas-tight stainless steel ball valves and Teflon-lined septa.

INTRODUCTION

The growing costs of traditional remediation techniques have helped foster a market for natural, less expensive, methods to clean contaminated sites [1]. As a result, additional research is mandated to effectively design and implement bioremediation technologies [2]. A major component of this research involves biological treatability tests and experiments to determine the kinetics of the reactions involved in contaminant destruction. This work is typically done using either small volume bottles, or continuous reactors [3, 4, 5, 6]. These systems have the advantage of simplicity, and are useful for measurement of degradation potential.

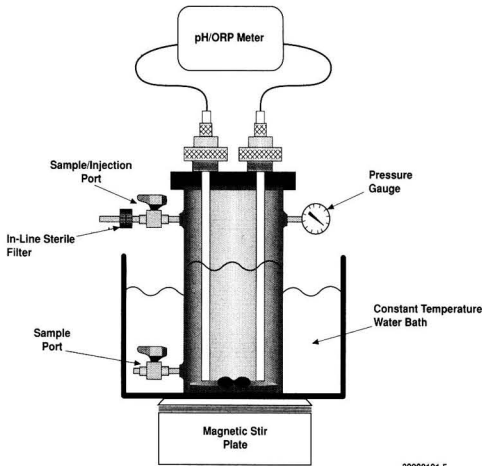
Using the traditional reaction vessels for monitoring process dynamics during biodegradation of volatile organic compounds has shown limitations. For example, small volume bottles limit the number of liquid samples that can be collected since the vessel usually contains 100 mL or less of media. Typically, several milliliters of media is required to measure the important aqueous properties. Multiple sacrificial bottles can provide the needed sample volume, but bottle-to-bottle differences add another source of experimental variation that complicates the analysis of process dynamics. In addition, these vessels are generally sealed using either septa or mininert valves, both of which can leak volatile compounds after being punctured several times [7, 8, 9]. This is particularly a problem

with microbial experiments in which a significant amount of gas is produced causing the pressure in the vessel to increase, thus, tending to force material out of the reactor. Furthermore, continuous measurement of internal parameters such as pH, oxidation/reduction potential (ORP), dissolved oxygen (DO), and temperature are impossible in these reactors since they cannot be fitted with probes to measure these properties.

In continuous reactor experiments, internal parameters may be easily measured, but important dynamic information is lost since only single point, steady state information can be obtained. This lost information includes parameter interactions, which are important to understanding the full reaction kinetics [10]. Additionally, sealing these reactors against the loss of volatile compounds is difficult since they require pumps and tubing to which the compounds may sorb and through which the compounds may escape. In this paper, data are presented that demonstrate a new experimental system that allows for detailed monitoring of process dynamics during biodegradation of volatile organics.

MATERIALS AND METHODS

The experimental reaction vessel and associated equipment is shown schematically in Figure 1. Engineering drawings of



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FIGURE 1. Schematic of the equipment used in the batch CCl_4 degradation experiments.

the reactor that indicate the location of sample and injection ports and reactor seals are shown in Figure 2. The reactor is a 1 L stainless steel vessel that is fitted with gas and liquid sampling ports, a 0-30 psi bourdon tube pressure gauge constructed entirely of stainless steel (McMaster-Carr, Santa Fe, CA), an *in situ* sterilizable pH electrode (Cole-Parmer, Chicago, IL), and an *in situ* sterilizable ORP electrode (Cole-Parmer, Chicago, IL). To minimize VOC sorption to surfaces in the reactor, all internal parts are constructed of stainless steel and glass. Viton o-rings are used, when necessary, to provide a positive seal and ensure that no gasses escape from the reactor. The portions of the pH and ORP electrodes that contact VOCs are made of glass. The electrodes are fitted to the reactor using housings with Viton seals (Cole-Parmer, Chicago, IL). All of the sampling and injection ports are equipped with Whitey 40-T series gas-tight stainless steel ball valves (Whitey Co., Highland Heights, OH). These valves have live-loaded packing to eliminate the need for packing adjustments after temperature cycling such as experienced during autoclave. A glass coated, magnetic stir bar (Fisher Scientific, Pittsburgh, PA) is used to ensure that the reactor contents are well mixed.

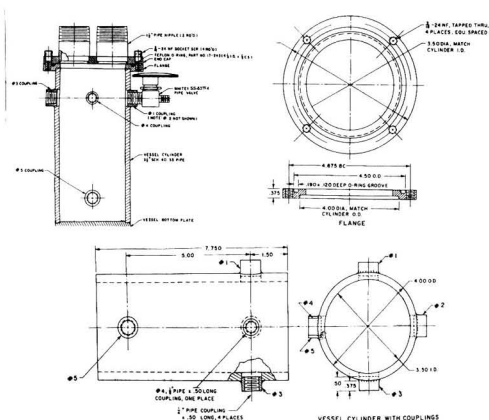


FIGURE 2. Engineering drawings describing the batch reactor.

To demonstrate the utility of this reactor, batch CCl_4 biodegradation experiments were performed under conditions which facilitated CCl_4 destruction and conditions which inhibited CCl_4 destruction. For these experiments, a bacterial consortium, isolated from the groundwater at the Department of Energy's Hanford Site, was exposed to CCl_4 under denitrification conditions. Before inoculation, the reactor was sterilized in an autoclave, charged with 750 mL of sterile, buffered simulated groundwater, and amended with nitrate. The concentrations of the major ions in the simulated groundwater were 46 mM Na^+ , 100 mM K^+ , 0.06 mM Ca^{+2} , 0.6 mM Mg^{+2} , 1.6 mM SiO_3^{-2} , 1.5 mM CO_3^{-2} , 0.04 mM SO_4^{-2} mM, 100 mM PO_4^{-2} , 1.3 mM Cl^- , and 194 mM NO_3^- . Next the reactor was pressurized to 10 psi with nitrogen gas and allowed to stand for 60 hours to test for gas leaks. A reduction in pressure would indicate a leak in the reactor. All leaks were alleviated before proceeding. Once the reactor passed the pressure test, the medium in the reactor was purged with nitrogen for 2 hours to deoxygenate the system, and sodium acetate (Sigma, St. Louis, MO) was added. The system was then charged with CCl_4 and biomass using appropriately sized Monoject syringes (Sherwood Medical Co., St. Louis, MO) equipped with custom made needles which were 20 cm in length. The initial levels of acetate, CCl_4 , and biomass for the experiment where CCl_4 was degraded were 400 ppm, 257 ppb, and 12 mg dry weight per L (mg-DW/L), respectively. The initial levels of acetate, CCl_4 , and biomass for the experiment where CCl_4 was not degraded were 800 ppm, 530 ppb, and 86 mg-DW/L, respectively.

Once inoculated, the reactor was placed in a constant temperature water bath that was maintained at 17°C, and mixed with a magnetic stir bar at 600 rpm. Periodically, the reactor pressure, temperature, pH, and ORP were recorded. To measure CCl_4 levels, 2.5 mL aqueous samples were removed from the reactor using a sterile syringe (Pressure Lok, Dynatech Precision Sampling Corp., Baton Rouge, LA), extracted in hexane, and later analyzed on a gas chromatograph equipped with an electron capture detector (Hewlett Packard, Palo Alto, CA). The detection limit for CCl_4 was approximately 10 ppb.

Anions and biomass were measured three times a day by withdrawing a 10-mL aqueous sample from the reactor using sterile, 20 mL Monoject syringes. Biomass levels were determined by optical absorbance. Here, approximately 4 mL of the 10-mL sample were sonicated for 30 sec and absorbance was then measured at 450 nm. From this absorbance reading, the dry weight of the biomass was determined from a standard curve. The remaining 6 mL of the sample were filtered through a 0.45- μm membrane to remove biomass. The filtrate was collected and analyzed on an ion chromatograph to determine acetate, nitrate, nitrite and sulfate concentrations.

To maintain the desired nitrate and acetate levels in the reactor, the first anion sample taken each day was analyzed and the amount of acetate and nitrate required to bring the aqueous solution in the reactor back to the desired level was added with a sterile syringe. The target levels of nitrate and acetate to maintain in the reactor for the experiment where CCl_4 was degraded were 100 ppm nitrate and 600 ppm acetate. The target levels of nitrate and acetate for the experiment where CCl_4 was not degraded were 1200 ppm nitrate and 300 ppm acetate.

In the abiotic tests, the above procedures were followed except that no biomass was injected into the reactor, and biomass concentrations were not determined. Additionally, in these abiotic tests, VOC concentrations were measured only once per day.

RESULTS

Figures 3 through 5 show the system parameters for a CCl_4 biodegradation experiment designed to obtain kinetic values.

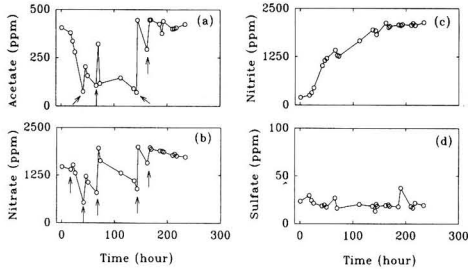


FIGURE 3. Anion concentrations versus time for an example experiment in which biodegradation of CCl_4 did not occur. (a) acetate, (b) nitrate, (c) nitrite, (d) sulfate.

For this experiment, reaction conditions were chosen to minimize CCl_4 destruction to demonstrate that the reactor can be operated for an extended-period of time (2 weeks) without VOC losses caused by sorption or gas leaks. This is clearly shown in Figure 5a, which gives the aqueous CCl_4 concentration as a function of time. The points represent the measured levels while the dashed line is the equilibrium level of CCl_4 predicted by Henry's law if no biotic or abiotic losses occurred. The predicted reduction in CCl_4 concentration shown on Figure 5a is a result of sampling and subsequent re-equilibration between the liquid and the gas phases.

The predicted CCl_4 equilibrium level was estimated by equation (1):

$$C_i = \frac{m_0 - \sum_i (C_{i,i} V_{\text{sample},i})}{V_l + V_g k_h} \quad (1)$$

where C_i is the aqueous CCl_4 concentration when the liquid and gas volumes of the reactor are V_l and V_g , respectively. The parameters $C_{i,i}$ and $V_{\text{sample},i}$ are the CCl_4 concentration and volume of aqueous sample removed from the reactor at the i th sampling period. The initial mass of CCl_4 added to the reactor, m_0 , was estimated from Henry's law by assuming that the aqueous concentration of CCl_4 measured after four hours was the initial equilibrium level. The Henry's law constant, k_h , at 17°C was estimated as $0.856 \text{ (mg/L gas phase)/(mg/L aqueous phase)}$ [11]. Equation (1) is applicable to this reactor system even though the pressure in the reactor is changing, because of sampling and gas generation by the microbes, since

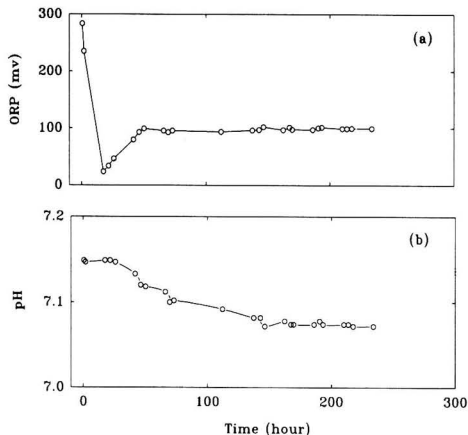


FIGURE 4. ORP (a) and pH (b) versus time for the example experiment.

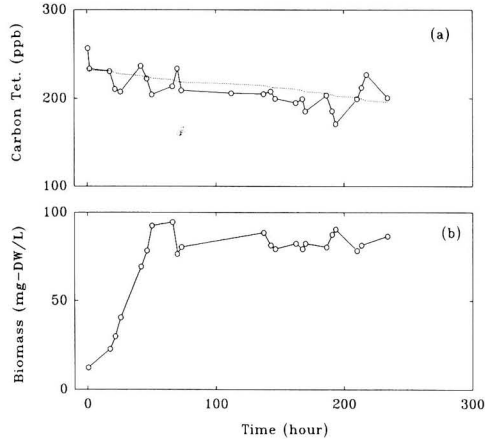


FIGURE 5. CCl_4 (a) and biomass (b) versus time for the example experiment.

Henry's law constants do not vary significantly within the range of pressures seen in these experiments (10 psi to 25 psi).

Besides the aqueous CCl_4 concentration, other important system parameters were also measured. These parameters include major anion concentrations (Figures 3a-d), ORP (Figure 4a), pH (Figure 4b), and biomass concentration (Figure 5b). The arrows on Figures 3a and 3b denote the times where acetate and nitrate were added to the reactor. As expected, the biomass used the acetate and nitrate in its growth and denitrification processes, and as a result nitrite was formed. Sulfate is not involved in denitrification, and hence remained constant.

Abiotic experiments were also conducted to demonstrate that the presence of biomass does not affect the performance of the reactor. Figure 6 shows the aqueous concentration of CCl_4 within the reactor fluid as a function of time for a 12 day experiment without biomass. With the exception of the initial partitioning of the CCl_4 , there is clearly no significant drop in CCl_4 concentration. Additional abiotic tests have been performed using trichloroethylene and similar results were obtained.

Figure 7 shows the CCl_4 concentration as a function of time for an experiment where CCl_4 was biodegraded to demonstrate the usefulness of the reactor in monitoring VOC destruction. Again, the points represent the measured levels while the dashed line is the equilibrium level of CCl_4 predicted by Henry's law if no biotic or abiotic losses occurred. It is evident from this figure that the CCl_4 concentration diminished throughout the duration of the experiment from a starting level of approximately 530 ppb to a final level of near 140 ppb. This represents biodegradation of 250 ppb since the predicted CCl_4 concentration if no biotic or abiotic losses occurred diminished to

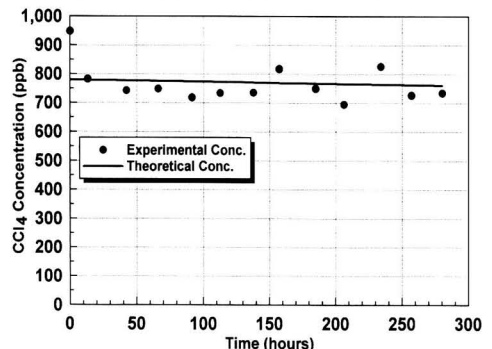


FIGURE 6. CCl_4 concentration versus time for an abiotic experiment.

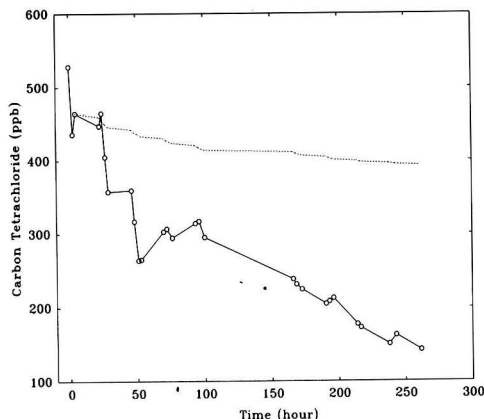


FIGURE 7. CCl_4 concentration as function of time in an experiment in which biodegradation occurred.

only 390 ppb. This data is presented to demonstrate the utility of this reactor system for obtaining system parameters that will allow the kinetics of the biodegradation process to be studied, not to demonstrate the conditions under which contaminant destruction is obtained. Examination of such conditions will be the subject of a later manuscript.

DISCUSSION

The reactor described in this paper allows the monitoring of important system parameters to enhance understanding of the dynamics of biological reactions involved in the destruction of volatile organics. The necessity of obtaining detailed information about the dynamic behavior of a reactor system has been universally understood, and exploited, in traditional reaction engineering for many years. Such information has provided the insights required to develop useful predictive models of the reaction kinetics. These predictions provide a significant portion of the basis for engineering design. For example, researchers employing biotechnology for other purposes have used this approach to develop a more detailed understanding of cellular processes [12, 13].

In the example experiments reported here, the reactor allowed for frequent measurement of anion, biomass, and CCl_4 concentrations so that the dynamics of the degradation process could be monitored. While these measurements were being taken, the pH, ORP, and pressure were also monitored using *in situ* sensors. In addition, the reactor could be easily modified to allow the continuous measurement of other system parameters such as temperature and DO. Although not used for the experiments reported here, the reactor is also equipped with a gas sampling port so that head space samples can be collected to confirm the material balance on volatile compounds.

One of the reasons that this reactor can be used to measure system dynamics is that many liquid samples can be collected. In the experiments reported in this paper, more than 50 liquid samples, having a total volume of nearly 300 mL, were removed from the reactor to determine the concentrations of biomass, CCl_4 , and anions. It is speculated that at least another 150 mL could be removed for analysis without impacting operation or the ability to sample the reactor. This ability to remove multiple samples without destroying the integrity of the seal is a result of the design of the sample/injection ports. In these ports, a stainless steel ball valve and a Teflon-lined septa are used to ensure that no gases escape the reactor. Because the ball valves can isolate the septa from the reactor contents, the septa can be changed after each sample. Another important attribute of

the valved port design is the ability to perform pre-experiment pressure tests to ensure the vessel is gas tight so that no volatile compounds will leak from the reactor.

ACKNOWLEDGMENTS

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Ex-Situ Forced Aeration of Soil Piles: A Physical Model

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This paper presents a physical model of a technology in its early stages of development, which is here referred to as "ex-situ forced aeration of soil piles," or, briefly, "soil pile aeration." The model can be used in a dual capacity. First, it can be used to screen the technology; that is, to determine if, based on soil characteristics and contamination levels, the technology is at all applicable. Second, if the technology is deemed applicable, the model can be used as a design tool to optimize the basic design parameters, which are the pile radius and length, and the vacuum blower characteristics. The physical model presented in this paper provides an useful framework for understanding the influence that the design and soil parameters have on the effectiveness and/or viability of the technology, and can be useful tool for preliminary design of aeration piles.

INTRODUCTION

This paper presents a physical model of a technology in its early stages of development, which is here referred to as "ex-situ forced aeration of soil piles," or briefly, "soil pile aeration." *Ex-situ* forced aeration of soil piles is used to stimulate the biodegradation of organic constituents by naturally-occurring soil microorganisms. The advantages of this approach over land treatment (a more conventional approach to the biodegradation of organics contained in soils) are that the treatment unit takes up less area and can be more economically contained. Also, the required treatment period may be reduced using soil pile aeration compared to land treatment because optimal treatment conditions (i.e., oxygen exchange, temperature maintenance) may be more readily achieved.

In this paper, the problem of uniformly aerating a semi-cylindrical soil pile whose length is much greater than its radius is considered. A slotted pipe, connected to a vacuum blower is assumed to be placed at one end of the pile, in the center of a semi-cylindrical soil pile, running along the length of the pile. A system of two coupled differential equations is derived, describing the induced air flow within the soil, and the induced flow within the centrally placed vacuum pipe. Based on a minimum required oxygen demand for the biological oxidation of the contaminant present in the soil, the model is able to

predict the radial air flow per unit length of pile, and the overall flow at the vacuum blower, as a function of the negative pressure at the blower, the physical dimensions of the pile (length and radius), and the soil permeability to air flow.

Thus, the model can be used in a dual capacity. First, it can be used to screen the technology. That is, to determine if, based on soil permeability and contamination levels, the technology is at all applicable. Second, if the technology is deemed applicable, the model can be used as a design tool to optimize the basic design parameters, which are the pile radius and length, and the blower characteristics.

The paper presents a complete derivation of all the equations necessary to describe an aerated pile system, together with a discussion of the assumptions made. The equations cannot be solved analytically, however, a program for their numerical solution has been developed. A discussion of the influence of all the parameters necessary to describe the system is presented. A case study illustrating the use of the model for design purposes is presented.

The physical model presented in this paper provides an useful framework for understanding the influence that the design and soil parameters have on the effectiveness and/or validity of the technology, and can be a useful tool for preliminary design of aeration piles.

DESCRIPTION OF THE TECHNOLOGY

Ex Situ forced aeration of soil piles involves the installation of a system of slotted pipes connected to a vacuum blower into a soil pile. A vacuum is exerted on the slotted pipe, which draws air through the soils and provides indigenous microorganisms with sufficient oxygen to degrade organic contaminants present in the soil.

Like conventional land treatment of hydrocarbon contaminated soils, contact with oxygen, nutrients, and carbon is the critical factor in the effectiveness of this technology. The advantage of forced aeration of soil piles over conventional land treatment is that the treatment unit takes up less area, and can be more economically contained. Also, the required treatment period may be reduced using soil pile aeration treatment as compared to land treatment, because optimal treatment conditions (i.e., oxygen exchange, temperature, etc.) can be more readily achieved. Soil pile aeration is closely related to the composting technology (see, for example, Savage, Diaz, and Golueke [1], and references therein). Even though the values of some operating parameters are different, the two technologies share the common problem of oxygen distribution and flow control, which is the focus of this paper.

The treatment units (soil piles) are provided with a containment system, which includes a bermed liner to reduce the potential for releases through leaching and run-off, and a cover to reduce infiltration of precipitation, volatilization, and wind-borne dust. The cover is installed in such a way as not to impede the flow of atmospheric air through the soil.

Construction of a forced aeration soil pile begins with the construction of the liner system, followed by placement of the soil to be treated onto the contained area. Soil conditioners, such as straw, sawdust, or manure can be added during soil placement to improve soil texture and increase the soil's permeability. Nutrients and moisture are also added at this stage to promote microbiological activity.

During placement of the soil, an aeration system is installed, consisting of a horizontal system of slotted pipes. Upon completion of soil placement, the slotted pipes are manifolded to vacuum blowers, which are sized to draw enough air through the soil to promote biodegradation.

In the following sections, the system briefly described above is modeled mathematically, and equations relating the vacuum at the blower to the air flow necessary for properly aerating a soil pile are derived.

DERIVATION OF THE AIR FLOW EQUATIONS

Introduction and Notation

We will consider the problem of aerating a semi-cylindrical soil pile whose length is much greater than its radius, placed over an impermeable surface (liner). A slotted pipe, kept at a pressure lower than atmosphere, is assumed to be placed centrally, on the bottom of the pile (Figure 1). The following notation will be used:

- L = length of pile (m)
- R = radius of pile (m)
- μ = air viscosity (Kg/m \cdot sec)
- k = soil permeability (cm 2 or m 2)
- R_w = radius of slotted pipe (m)
- P_w = Negative of gauge pressure (vacuum) in the pipe (Kg/m \cdot sec 2)

We will use the convention of using gauge pressure (that is, differences between pressure and atmospheric pressure). We will also take pressures below atmospheric pressure to be positive. In this convention, flow occurs from low to high values of P (or the flow velocity is proportional to ∇P , rather than $-\nabla P$).

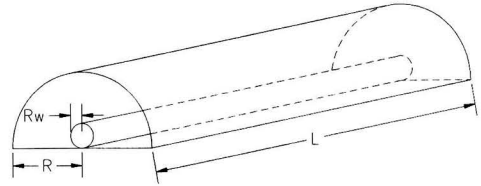


FIGURE 1. Aeration pile geometry.

Air Flow into a Slotted Pipe Under Ideal Conditions

In the ideal case in which:

- the pile is infinitely long ($L \rightarrow \infty$),
- the pressure in the slotted pipe is constant and uniformly distributed along the pipe, and
- there is no head loss for air entering the pipe;

the problem of aerating a semi-cylindrical soil pile can be analyzed rather simply, and is equivalent to one solved by Muskat [2]. For this simplified case the problem is one-dimensional, and all quantities are dependent on the single variable r , the radial distance from the center of the pile (there is no dependence on the horizontal position along the pipe).

For the problem described above, the air flux within the soil pile (m 3 air/m 2 ·sec) is given by:

$$v(r) = \frac{k}{\mu r} \frac{P_w}{\ln(R/R_w)} \quad (1)$$

where $v(r)$ represents the radial (and only) component of the air flux, which is directed radially toward the pipe. The total flow of atmospheric air entering the pile is obtained by integrating the air flux over the external area of the soil pile. Since the pile is assumed to be of infinite length, this flow is infinite. A more physically significant quantity is the air flow per unit horizontal length of pile, q (m 3 air/m \cdot sec), which will be termed the pile's specific flow. This quantity is given by:

$$q = \int_0^\pi v(r=R) R d\theta = \left(\frac{\pi k}{\mu} \right) \frac{P_w}{\ln(R/R_w)} \quad (2)$$

It should be noted that, by mass balance, q also equals the flow per unit length of slotted pipe entering the pipe.

Even though equation (2) is only valid for an infinitely long pile, it should be considered as a good approximation, as long as the horizontal dimension of the pile is greater than its radius, which is often the case in field applications.

Air Flow into a Slotted Pipe Under Field Conditions

Equation (2) neglects two effects: horizontal pressure gradients within the pipe, and entry head loss for air entering the pipe through the slots. The first assumption, in particular is somewhat unrealistic, because what drives the flow within the pipe, toward the blower, is a pressure gradient whose magnitude increases with the air flow. As will be shown in the following, horizontal pressure gradients within a slotted pipe can be quite significant. The second effect is due to the fact that a slotted pipe is only open to flow over a large number of thin slots. Thus, air flowing toward the central slotted pipe must enter these thin slots, and thus it experiences an entry pressure loss in traveling from the soil through a slot to the pipe.

In analyzing field systems, both effects should be included. These effects will lead to a pressure and flow distribution within the pipe, which will be determined in the next sections.

Equations for a Pile of Finite Length

In the following, it will be assumed that the basic form of equation (2) is still valid, however, due to the pressure distribution within the pipe, both the specific flow, q , and the slotted pipe pressure, P_w , will be now considered to be a function of x , the distance along the pipe.

We will consider a situation in which a negative pressure (vacuum) P_w is applied at the far end of the pipe ($x=L$). We will determine the flow per unit length of the pipe, $q(x)$, the total air flow along the slotted pipe, $Q(x)$, and the pressure, $P(x)$ (see Figure 2) as a function of the horizontal coordinate along the pile.

The following notation is used:

$P(x)$ = pressure along the pipe (Kg/m²-sec²);

$q(x)$ = specific flow (flow into the pipe, per unit length of pipe, m³/m²-sec); and

$Q(x)$ = total flow along the pipe (m³/sec).

Since the horizontal flow along the pipe is due to the air flow entering the pipe radially, by conservation of mass we have that:

$$Q(x) = \int_0^x q(y) dy \quad (3)$$

By taking the derivative of equation (3), we obtain that:

$$q(x) = \frac{dQ(x)}{dx} \quad (4)$$

From equation (3), the boundary condition on $Q(x)$ is:

$$Q(x=0) = 0 \quad (5)$$

Equation (4) relates the specific flow into the pile to the flow along the pile. In order to determine these two quantities, equations must be derived that relate $q(x)$ and $P(x)$. This is done in the following two sections.

Entry Pressure Loss

Equation (2) was derived assuming that there is no air pressure drop in entering the pipe, so that the air pressure just inside the pipe equals the air pressure just outside the pipe. In a real system, however, the loss of vacuum entering the pipe must be considered. We will indicate such vacuum loss by $\Delta P(x)$. Since what drives the flow from the periphery of the pile toward the pipe is the pressure differential between atmospheric pressure and the pressure just outside the vacuum pipe, the term P_w in equation (2) must now be replaced by $(P - \Delta P)$, which (since P is the pressure inside the pipe), represents the pressure just outside the pipe. With this in mind, and taking into account the x -dependence of all quantities, we can rewrite equation (2) as:

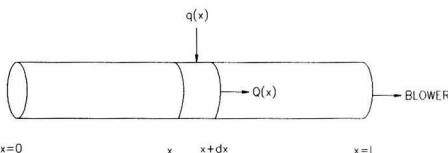


FIGURE 2. Schematic of flow into the slotted pipe.

$$q(x) = \left(\frac{\pi k}{\mu} \right) \frac{(P(x) - \Delta P(x))}{\ln(R/R_w)} \quad (6)$$

Entry head loss is described in terms of a dimensionless empirical constant of order unity, K , as:

$$\Delta P(x) = K \rho \frac{v^2(x)}{2} \quad (7)$$

where $v(x)$ represents the air entry velocity into a slot (m/sec), and ρ represents the air density (Kg/m³). For a circular orifice, it can be shown that K equals approximately 2.5. A value of $K=3$ is assumed for rectangular slots. It should be noted that the value of K is relatively insensitive to the shape of the opening and that air pressure drops over the opening are generally small relative to the vacuum in the pipe. It is thus believed that the value of K used is adequate for this modeling exercise.

The velocity $v(x)$ can be related to the specific flow $q(x)$ since:

$$\text{Velocity} = \frac{\text{Air Flux Into Pipe}}{\text{Entry Area}} \quad (8)$$

Consider a segment of pipe of length dx . The flow entering the pipe is simply the product of dx times the specific flow, $q(x)$. If we define f as the fraction of the area of pipe open to air flow, the overall area open to flow is given by $2\pi * R_w * dx * f$. Thus, the air entry velocity $v(x)$ is given by:

$$v(x) = \frac{q(x) dx}{2\pi R_w dx f} = \frac{q(x)}{2\pi R_w f} \quad (9)$$

By use of equation (9), we can rewrite equation (7) as:

$$\Delta P(x) = \frac{K \rho}{8\pi^2 f^2} \frac{q^2(x)}{R_w^2} \quad (10)$$

and equation (6) as:

$$q(x) = \frac{\pi k}{\mu} \frac{1}{\ln(R/R_w)} \left[P(x) - \frac{K \rho}{8\pi^2 f^2} \frac{q^2(x)}{R_w^2} \right] \quad (11)$$

By defining:

$$a = \frac{\pi k}{\mu} \frac{1}{\ln(R/R_w)} \quad (12)$$

$$b = \frac{K \rho}{8\pi^2 f^2} \frac{1}{R_w^2} \quad (13)$$

and solving equation (11) for $q(x)$, we obtain:

$$q(x) = \frac{1}{2ab} \left[\sqrt{1 + 4a^2 b P(x)} - 1 \right] \quad (14)$$

Finally, by use of equation (4), we can write the following differential equation relating the flow along the pipe to the pipe vacuum:

$$\frac{dQ(x)}{dx} = \frac{1}{2ab} \left[\sqrt{1 + 4a^2 b P(x)} - 1 \right] \quad (15)$$

It should be noted that the flow of fluids in a manifold is a problem similar to that discussed in this section, and is

addressed in Bird et al. [3] (Problem 7.Q₄ Flow Distribution in Manifolds). A complete solution of the manifold problem can be found in Acrivos et al. [4].

Pressure Gradient Along the Pipe

In the following, we will determine the vacuum loss along the pipe, essentially due to frictional forces. Such vacuum loss depends on the flow regime, which can be laminar or turbulent. This topic is addressed in Bird et al. [3], and will be briefly summarized here.

For low velocities, such that the Reynolds number $Re = V * 2 * R_w * \rho / \mu < \approx 2000$, where V represents the air velocity along the pipe, the flow is laminar, and the pressure drop is proportional to Q , and is given by:

$$\frac{dP}{dx} = \frac{8\mu Q(x)}{\pi R_w^4} \quad (16)$$

In the turbulent regime, experimental results indicate that the pressure drop is proportional to a higher power of Q , close to Q^2 , depending on the roughness of the tube.

Even though the slotted pipes used for aerating soil piles are smooth, the flow component perpendicular to the axis of the pile should create a high degree of turbulence, effectively mimicking the effect of a large degree of roughness in the tube (Figure 3).

For the turbulent regime, we will thus use an expression for the pressure drop appropriate to high Reynolds number, high roughness, which is:

$$\frac{dP}{dx} = \frac{\lambda \rho Q^2(x)}{\pi R_w^5} \quad (17)$$

where λ represents an empirical friction factor. Equation (17) implies that the friction factor, f , presented in Figure 6.2-2 of Bird et al. [3] is assumed to be constant, and equal to λ/π .

In order to avoid discontinuities in the dP/dx vs $Q(x)$ relationship, which are physically unrealistic and would hinder the numerical solution of the pressure and flow equations, the value of Q at which the laminar-turbulent transition occurs is determined by setting equation (17) and equation (16) equal, and solving for Q . The value of the air flow at which the transition from laminar to turbulent flow occurs is thus determined to be:

$$Q^{TRANS} = \frac{8 \mu R_w}{\lambda \rho} \quad (18)$$

The value of λ can be estimated from Figure 6.2-2 of Bird et al. [3] to be approximately equal to $0.01/\pi = 0.0032$. It

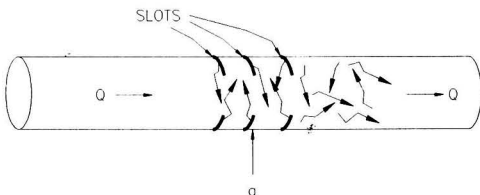


FIGURE 3. Effects of perpendicular air flows within a slotted pipe.

should be noted that experimental verification of the value of λ for air for slotted pipes used in aeration pile applications is presently lacking.

In summary, we have derived the following expressions for the pressure drop along the pipe.

$$Q < Q^{TRANS}: \frac{dP}{dx} = \frac{8\mu Q(x)}{\pi R_w^4} \quad (19)$$

$$Q > Q^{TRANS}: \frac{dP}{dx} = \frac{\lambda \rho Q^2(x)}{\pi R_w^5} \quad (20)$$

The relationship between dP/dx and $Q(x)$ is shown graphically in Figure 4. This figure was created using the above derived value for λ , a value of the air density equal to 1.2 kg/m^3 , and a value of the air viscosity equal to $1.8 * 10^{-5} \text{ kg/m} \cdot \text{sec}$ [5]. Figure 4 indicates that the pressure loss along the slotted pipe is a strong function of the pipe radius and that, for small diameter pipes, the pressure loss can be significant at flows as low as 10 to 30 cfm (0.0047 to $0.0142 \text{ m}^3/\text{air}/\text{sec}$).

Summary of the Air Flow Equations

In the previous sections, we have derived a set of equations describing the relationship between flow and pressure within a slotted pipe for aerating soil piles. These equations, which must be solved simultaneously, are summarized below:

$$\frac{dQ(x)}{dx} = \frac{1}{2ab} \sqrt{1 + 4a^2 b P(x)} - 1 \quad (21)$$

$$\frac{dP(x)}{dx} = \frac{8\mu Q(x)}{\pi R_w^4} \left(Q(x) < \frac{8 \mu R_w}{\lambda \rho} \right) \quad (22)$$

$$\frac{dP(x)}{dx} = \frac{\lambda \rho Q^2(x)}{\pi R_w^5} \left(Q(x) > \frac{8 \mu R_w}{\lambda \rho} \right) \quad (23)$$

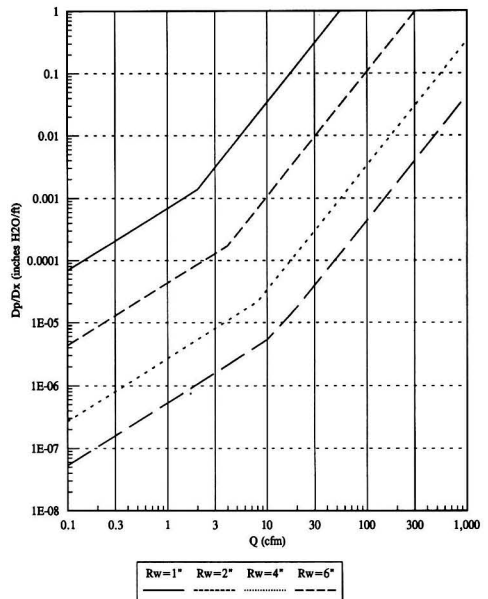


FIGURE 4. Pressure drop along slotted pipe as a function of air flow.

where:

$$a = \frac{\pi k}{\mu} \frac{1}{\ln(R/Rw)} \quad (24)$$

$$b = \frac{K\rho}{8\pi^2 f^2} \frac{1}{Rw^2} \quad (25)$$

$$\lambda = 0.0032 \quad (26)$$

Boundary Conditions

In order to solve the system of equation (21) through equation (23), boundary conditions on Q and P must be specified. The simplest way to specify boundary conditions is to specify Q and P at the far end of the pipe ($x=0$) (opposite to the blower).

At $x=0$, according to equation (5), we always have $Q(x=0)=0$, while the value of the pressure at the far end of the pipe $P(x=0)$ must be specified according to design requirements. Typically, however, one is interested in specifying a minimum value of the specific flow, q_0 , that will meet the aeration requirement of the soil pile. Such value can be turned into a minimum value of the pressure, P_0 , by solving equation (11) for P_0 as follows:

$$P_0 = q_0 \left(\frac{1}{a} + bq_0 \right) \quad (27)$$

The value of P_0 so obtained should be used as the pressure boundary condition at the far end of the pipe ($P(x=0)$).

Once the pressure and flow boundary conditions have been specified, equation (21) through equation (23) can be integrated between $x=0$ and $x=L$. The integration yields the value of pipe pressure and flow at any point along the pipe, and, in particular, it determines the total air flow into the blower ($Q(L)$), and the vacuum ($P(L)$) required at the blower end of the slotted pipe. These values should be interpreted as the blower vacuum necessary to achieve the specified specific flow-rate at the far end of the pipe, and the overall flow of air into the blower. This information can be used to size the blower. In general, devices to protect the blower, such as a filter and a de-mister would be installed between the slotted pipe header and the blower. These devices are liable to induce vacuum losses in the air line, so that $P(L)$ does not necessarily equal the blower vacuum. The value of the specific flow, $q(x)$, at

any point along the length of the pile is obtained by using equation (14) and the calculated value of $P(x)$.

SOLUTION OF THE AIR FLOW EQUATIONS

Parameters Necessary for the Solution

Equation (21) through equation (23) cannot be solved analytically, however, a computer program was written that solves them and plots the results obtained for $P(x)$, $q(x)$, and $Q(x)$. The input parameters necessary to effect the solution of equation (21) through equation (24) are listed in Table 1. It should be noted that, for ease of use, some parameters in the computer program are to be specified in the American System of units. The parameters in Table 1 are briefly discussed below.

Geometry of the System

The radius and length of the pile, R and L , are system specific. Typical values are $R=10$ ft (3 m) and $L=100$ ft (30 m). In order to minimize frictional pressure losses, the radius of the slotted pipe, Rw , should be as large as possible. Slotted pipes typically used in aeration piles applications have a diameter of 4 inches (0.1 m), or $Rw=2$ inches (0.05 m). The fraction of area open to air flow, f , can be obtained from the manufacturer of the pipe. Typical values range between 0.2 percent and 0.3 percent. In order to minimize entry pressure losses, f should be chosen as large as possible.

Soil Property

The soil permeability, k , is a crucial parameter for the successful application of the soil pile aeration technology. Permeability is a measure of the ability of a porous medium to allow fluid flow, and is an intrinsic property of the porous medium. This parameter has dimension of [length²] and is approximately proportional to the square of the average pore size of the medium [5, 6, 7]. Permeability values are very much soil dependent, and vary between 10^{-5} cm² for gravelly soils, to lower than 10^{-13} cm² for glacial till [6].

Air Properties

The air viscosity and density, are function of pressure and temperature. At standard pressure and temperature, air viscosity equals approximately 1.8×10^{-5} kg/m·sec, and air density equals approximately 1.2 kg/m³ [8].

Table 1 Parameters Necessary for the Solution of the Air Flow Equations

GEOMETRY OF THE SYSTEM			
Description	Symbol	Base Case Value	Units
Radius of the Pile	R	10	ft
Radius of the Slotted Pipe	Rw	2	in
Length of the Pile	L	100	ft
Fraction of Pipe open to Air Flow	f	0.002	
SOIL PROPERTIES			
Soil Permeability	k	1.0E-08	cm ²
AIR PROPERTIES			
Air Viscosity	μ	1.8E-05	kg/m·sec
Air Density	ρ	1.2	kg/m ³
EMPIRICAL PARAMETER			
Head Loss Coefficient	K	3	
INITIAL CONDITION			
Specific Discharge at Far End of Pipe	q_0	0.5	cfm/ft

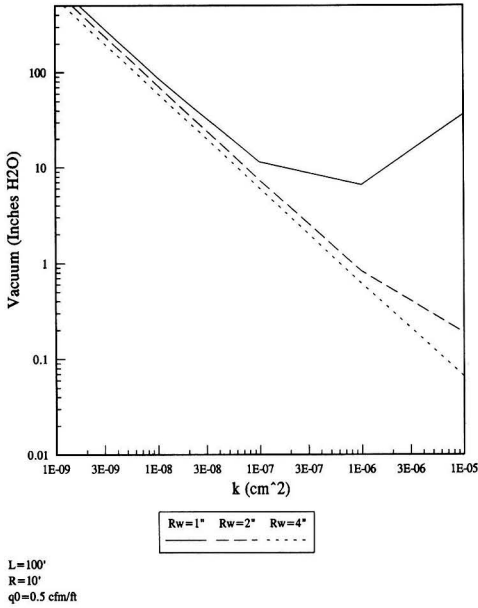


FIGURE 5. Vacuum at the blower end of the pipe as a function of soil permeability.

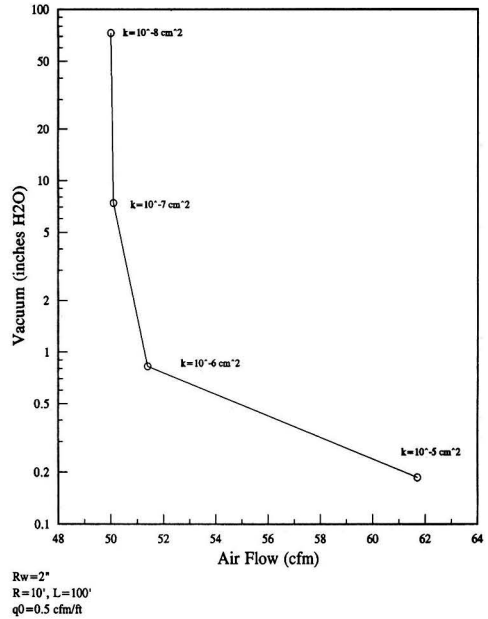


FIGURE 6. Air flow and vacuum at the blower end of the pipe as a function of soil permeability.

Empirical Parameter

The head loss coefficient for entry pressure loss is an empirical parameter of order unity [9].

Initial Condition

As discussed in the previous section, the value of specific flow (q_0) or of pressure (P_0) at the end of the pile opposite to the blower must be specified to integrate the air flow equations. From a design point of view, it is more useful to specify the value of q_0 , because this value is directly related to the oxygen demand for the oxidation of the organics contained in the soil. Since the vacuum in the slotted pipe decreases with distance from the blower, the end of the pipe opposite to the blower is the area subject to the lowest vacuum. In other words, the vacuum in the slotted pipe increases from its value at the opposite end of the blower ($x=0$) to its value at the blower ($x=L$) over the length of the slotted pipe. Thus the end opposite to the blower is the area with the lowest vacuum and, consequently, with the lowest specific flow. The value of q_0 should be chosen so as to meet the oxygen demand of the organics contained in the soil. Since q_0 is the lowest value of the specific flow achievable throughout the pile, this choice of q_0 will insure that the oxygen demand is met throughout the pile.

The value of specific flow that meets the oxygen demand of the organics contained in the soil is a function of the radius of the pile, of the level of contamination in the pile, and of the time over which remediation is to be achieved (see "An Example"). A simple calculation shows that values of q_0 between 0.1 and 1 cfm per linear foot of pile (1.55×10^{-4} to 1.55×10^{-3} m³air/m·sec) should in general be sufficient to aerate the soil. As will be shown in the following section, depending on the soil permeability these values may or may not be practically achievable.

Influence of Various Parameters on Aeration Pile Design

The main design parameters for aeration piles are the soil permeability, k , the pile's radius and length (R and L), and the slotted pipe radius (R_w). In the following, we address the effects of varying these parameters, and discuss these effects from a design point of view.

Soil Permeability (k)

Soil permeability (k), generally expressed in cm², is a property of the soil which relates to the soil's ability to allow the flow of a fluid, air in this case.

Figure 5 shows the vacuum pressure required at the blower end of the slotted pipe to achieve a specific flow of at least 0.5 cfm/ft (7.75 m³air/m·sec) throughout a pile of 10 ft (3 m) radius and 100 ft (30 m) length.

Two types of effects influence the required vacuum. The first is that, for the same pressure gradient, air flow is proportional to k . This means that the higher the value of k , the lower the vacuum required to meet the aeration requirement. The second effect is the vacuum loss due to air flow through the slotted pipe, toward the blower. This effect is minor in pipes of 2 inch (0.05 m) and 4 inch (0.1 m) radius, and is reflected in the fact that the curve referring to the 4 inch (0.1 m) pipe is slightly below the curve referring to a 2 inch (0.05 m) pipe in Figure 5. However, for smaller radius pipes, where the transition to turbulence flow occurs at lower flows and as a consequence, vacuum losses per foot of pipe are greater (see Figure 1), this effect can be important. Figure 5 indicates that, for a 1 inch (0.025 m) radius slotted pipe, the blower vacuum requirements start increasing for permeabilities greater than approximately 10^{-7} cm². This is due to the fact that, as k decreases, the induced flow through the slotted pipe increases

and, consequently, the pressure drop along the pipe also increases. Thus, to maintain a fixed value of vacuum at the far end of the pile opposite to the blower, much larger values of vacuum are required at the blower end. In this case, aeration of the pile would be far from uniform, with the end close to the blower receiving a higher specific flow of air (and, thus, better aeration) than the end opposite to the blower.

Figure 6 shows the relationship between vacuum at the blower end of the slotted pipe and air flow for various values of k . The figure shows that, for the range of k values likely to be of interest ($10^{-8} \text{ cm}^2 < k < 10^{-6} \text{ cm}^2$), air flow is a relatively constant (it is basically dictated by the aeration requirement at the far end of the pile), while the required vacuum decreases steeply with increasing permeability. It should be noted that the curve presented in Figure 6 is particularly useful for design because it can be superimposed on blower performance curves to identify the most appropriate blower for aeration of the pile in object.

From a design standpoint, there are two main conclusions to be drawn from the analysis presented above. The first one is that aeration pile technology is likely to be applicable for soils with a k value of 10^{-8} cm^2 or greater. The second one is that, if improperly sized, the radius of the slotted pipe can have a large influence on the vacuum requirements at the blower, and should be designed as large as possible.

Soil Pile Length (L)

The effect of varying the soil pile length on the required vacuum and induced air flow is shown in Figure 7. The top graph shows that, for a 2 inch (0.05 m) radius slotted pipe, the required vacuum is independent of the pile length for k values below 10^{-6} cm^2 (it is, however, strongly dependent on the value of k). This is due to the fact that at permeabilities less than 10^{-6} cm^2 , the flow into the slotted pipe incrementally induced along the pipe length is low enough that no significantly frictional vacuum loss occurs along the pipe. At higher permeabilities, higher flows per unit pipe length are induced, and flow increases sharply as a function of distance from the end opposite to the blower. For pipe lengths over approximately 100 ft (30 m) air flows become high enough that frictional vacuum losses become significant at the end closer to the blower. As a consequence, in order to maintain a fixed value of q_0 at the end of the pipe opposite to the blower, sharply increasing values of vacuum are required as the pile length increases.

This effect is clearly shown in the bottom graph in Figure 7, which presents the induced air flow into the blower necessary to achieve the specified value of q_0 at the end of the pipe opposite to the blower, as a function of pile length. It should be noted that in this graph, the value of the vacuum at the blower end of the pipe required to obtain the indicated value of q_0 increases with decreasing values of k . For permeabilities less than 10^{-6} cm^2 , air flow increases essentially linearly with pile length, indicating that $q(x)$ is constant along the pipe, and frictional vacuum losses are negligible. For permeabilities greater than 10^{-6} cm^2 , the induced flow builds up quickly along the pipe's length and vacuum losses accumulate, requiring high flow and vacuum levels to maintain a fixed value of q_0 at the end of the pile opposite to the blower. In the top curve of the bottom Figure 7, most of the flow into the blower comes from an area near the blower end of the pile, which is thus much more aerated than the end opposite to the blower.

Figure 7 clearly shows that, for likely operating conditions ($Rw = 2$ inches (0.05 m), k is approximately equal to 10^{-7} cm^2 , $L < 100$ ft (30 m)), vacuum losses along the length of the slotted pipe are minor. This implies that the value of the vacuum at the blower is uniformly propagated for the whole length of the pipe, and that, therefore, aeration is uniform throughout the pile. The air flow into the pile is independent of soil perme-

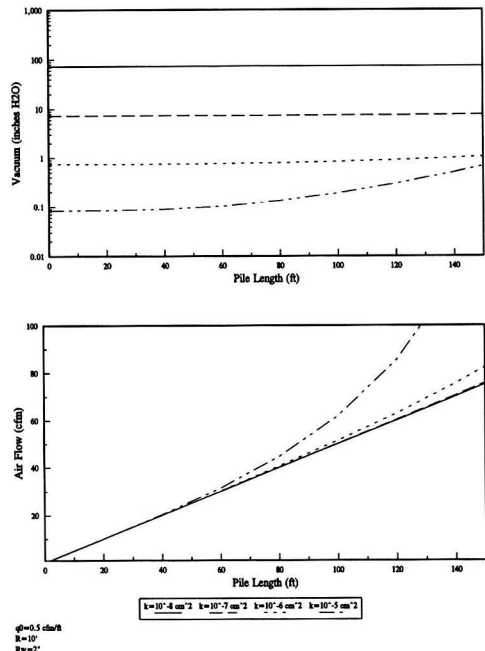


FIGURE 7. Blower end vacuum and air flow as a function of soil pile length.

ability, and increases linearly with pile length. Again, this means that the specific flow is constant throughout the pile. For these operating conditions, the air flow into the blower can be closely approximated as:

$$Q(L) = q_0 * L \quad (28)$$

where:

- $Q(L)$ = air flow into the blower (cfm or $\text{m}^3/\text{air}/\text{sec}$),
- q_0 = specific flow at the opposite end of the blower (cfm/ft or $\text{m}^3/\text{air}/\text{m}\cdot\text{sec}$), and
- L = length of the pile (ft or m).

On the other hand, the value of vacuum at the blower necessary to maintain the specified flow is inversely proportional to the soil permeability, meaning that low permeability soils will require higher vacuums than higher permeability soils.

Soil Pile Radius (R)

The effect of varying the pile radius is shown in Figures 8 and 9. These figures were generated by keeping constant the aeration requirement per unit volume of soil. This quantity is proportional to R^2 . It was assumed a value of the minimum specific flow (q_0) for a 10 ft (3 m) radius pile is 0.5 cfm/ft ($7.75 * 10^{-4} \text{ m}^3/\text{air}/\text{m}\cdot\text{sec}$). The value of q_0 for piles of different radius was scaled proportionally to R^2 . So, for example, for a 1 ft (0.3 m) radius pile, the value of q_0 was taken as $0.5 * (1/10)^2 \text{ cfm}/\text{ft} = 0.005 \text{ cfm}/\text{ft}$ ($7.75 * 10^{-6} \text{ m}^3/\text{air}/\text{m}\cdot\text{sec}$).

Figure 8 shows that the required vacuum at the blower end of the slotted pipe increases rather steeply with the pile radius. For a pile radius of 10 ft (3 m) or greater, this figure reiterates the conclusion previously drawn that values of k greater than 10^{-8} cm^2 are required. In fact, the horizontal line, which rep-

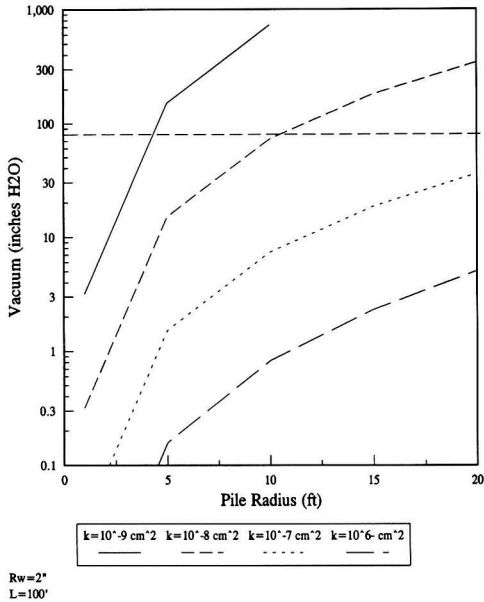


FIGURE 8. Required vacuum at the blower end of the pipe as a function of soil pile radius

resents a vacuum pressure of 80 inches of water column (0.2 atm), which is the maximum achievable with commonly available blowers, intersects the curve relative to the $k = 10^{-8} \text{ cm}^2$ case at a value of the pile radius of approximately 10 ft (3 m). If the soil to be treated has a permeability of 10^{-8} cm^2 or less, in order for the aeration pile technology to be applicable, smaller values of the radius must be chosen. It should be noted that, for a fixed volume of the soil to be treated, the land requirement for the soil treatment unit is approximately inversely proportional to the pile radius. This means that, by reducing the radius of the pile, one increases proportionally the land requirement for the treatment of the soil volume.

Finally, Figure 9 shows that, for the permeability range considered ($10^{-9} \text{ cm}^2 < k < 10^{-6} \text{ cm}^2$), the air flow at the blower is a strong function of the pile radius, but it is essentially independent of the soil permeability, being dictated exclusively by the aeration requirement (specific flow) at the end of the pile opposite of the blower.

Conclusions

The simulations discussed above indicate that the main parameter relevant to the design of a soil aeration pile is the permeability of the soil to be treated. Rather permeable soils are required for this technology to be applicable. A value of $k = 10^{-8} \text{ cm}^2$ (typical of silty sandy soils) seems to be the cutoff point. For permeabilities lower than 10^{-8} cm^2 , the vacuums required to maintain sufficient air moving through the soil are too high for aeration pile technology to be effective.

While on one hand it is desirable to achieve as high air flows as possible through the pile and along the slotted pipe, on the other hand, it is important to keep air flows low enough that vacuum losses along the pipe be low. The development of large vacuum gradients along the slotted pipe leads to non-uniform aeration of the pile, which results in high vacuum at the blower end of the slotted pipes in order to meet a minimum aeration requirement at the end of the pile opposite to the blower. The

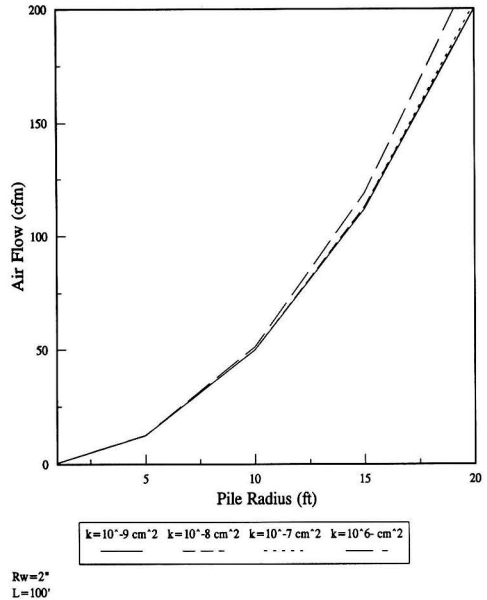


FIGURE 9. Air flow as a function of soil pile radius.

information presented above indicates that under normal operating conditions, vacuum losses along the slotted pipe should not be significant. However, to insure that this is indeed the case, it is suggested that the slotted pipe be designed with as large a diameter as possible.

Under operating conditions resulting in moderate air flows and negligible vacuum losses along the slotted pipe, the required vacuum is not a function of pile length. For values of the soil permeability of approximately 10^{-7} cm^2 , blower vacuums of the order of 10 inches of water column (0.025 atm) should be adequate to achieve a satisfactory aeration of the pile. These values are easily achievable by means of regenerative blowers. The pile length (L), however, affects the air flow at the blower, which increases linearly with L . If vacuum losses along the pile are negligible, the air flow into the blower can be estimated to be equal to $q_0 * L$, where q_0 represents the minimum air flow required per unit length of soil pile necessary to meet the oxygen demand for the biodegradation of the organics present in the soil. For piles of length on the order of 100 ft (30 m), and radius of order 10 ft (3 m), it is estimated that air flows between 10 and 100 cfm (0.0155 and 0.155 $\text{m}^3/\text{air}/\text{sec}$) are necessary for adequate aeration of the soil.

The required vacuum at the blower end of the slotted pipe and air flow are an increasing function of the pile radius. This is basically due to the fact that the aeration requirement, and hence the value of q_0 increases as the square of the radius. Thus, for larger radii, larger air flows are required to satisfactorily aerate the pile. By designing piles of small radial dimensions, blower requirements (vacuum and flow) decrease. However, since land requirements are approximately proportional to the inverse of the pile radius, they increase with decreasing radius. Thus, if the pile radius is too small, it can become a limiting factor in the design of a soil pile system.

Finally, it should be kept in mind that the system studied and modeled in this paper is the simplest aeration pile design, and it is possibly not adequate for all remedial applications. A number of variations on the basic design presented here are possible, such as having more than one slotted pipe kept under vacuum, or installing the blower in the middle of the pipe rather than at one end of it. However, the system modeled shares the basic features common to more complex soil pile

aeration designs, and as such it provides a useful tool for screening the technology and for preliminary design of aeration piles, as will be demonstrated in the next section.

SIMPLIFIED DESIGN EQUATIONS

The preceding sections addressed the theoretical development of equations describing a soil pile system, and the application of a computer model designed to solve them. This section discusses a simplified solution of the air flow equations, and develops the basis for the design of soil aeration piles. It should be noted that, for ease of treatment, the following discussion is presented in the SI system of units.

Simplified Equations

The computer runs presented in the previous section indicate that, under recommended operating conditions (negligible vacuum loss along the slotted pipe and consequent uniform aeration of the pile), the air flow induced at the blower and vacuum at the blower end of the pipe can be closely be approximated by:

$$Q = q_0 * L \quad (29)$$

$$P_w = \frac{\mu q_0}{\pi k} \ln \left(\frac{R}{R_w} \right) \quad (30)$$

where P_w and Q represent, respectively, the vacuum at the blower end of the slotted pipe and the induced flow at the blower. All other variables were defined previously. The total air flow necessary for aeration of semicylindrical soil pile, is given by:

$$Q = \frac{MV * OD * \left(\frac{1}{2} \pi * R^2 * L * C_0 * \rho_{soil} \right)}{V_{O_2} * MW * E * T} \quad (31)$$

where:

- Q = overall air flow (L_{air}/day);
- MV = molecular volume of $O_2 = 22.4 L O_2/mole O_2$ at STP;
- OD = oxygen demand for biodegradation of the organics (chemical specific, conservatively estimated at 3.5 g O_2/g organics);
- R = soil pile radius (m);
- L = soil pile length (m);
- C_0 = organics concentration in soil (g organics/Kg soil);
- ρ_{soil} = soil density (Kg soil/ m^3);
- V_{O_2} = fraction of O_2 in air by volume = 0.2 $L O_2/L$ air;
- MW = molecular weight of $O_2 = 32 g O_2/mole O_2$;
- E = efficiency of oxygen utilization, assumed to be 0.1 or 10 percent; and
- T = treatment time (days).

The specific flow, q_0 is given by:

$$q_0 = \frac{Q}{L} = \frac{MV * OD * \left(\frac{1}{2} \pi * R^2 * C_0 * \rho_{soil} \right)}{V_{O_2} * MW * E * T} \quad (32)$$

The above equations apply to a semi-cylindrical soil pile, outfitted with a single slotted pipe, and with a blower connected

at one end of the pipe. A number of possible design variations exist, mainly having to do with the number of slotted pipes used, and on the location of the blower connection with the slotted pipes.

Design Basis

In this section, the basis of design for the treatment of an arbitrary soil volume is presented. The basic design of the system considered involves a variable number soil piles, and a variable number of slotted pipes, connected in parallel to a collection header. Each pile is assumed to be outfitted with a blower connected to the collection header at one end of the pipe. Equations are derived relating the vacuum required at each blower and the air flow at the blower with the piles dimensions and number, with the number of slotted pipes to be installed within each pile, and with the dimensions of the area necessary for treatment. The relationships derived constitute a complete set of equations that enable the designer to properly size the equipment and dimension of the piles, and to estimate the land requirements for treatment.

If V_{tot} represents the volume of soil to be treated, the overall aeration requirements are calculated as:

$$Q_{tot} = \frac{MV * OD * (V_{tot} * C_0 * \rho_{soil})}{V_{O_2} * MW * E * T} \quad (33)$$

where all quantities have been previously defined. Assuming that a number of N_p of piles are utilized, the flow required for each pile is given by:

$$Q_{pile} = \frac{Q_{tot}}{N_p} \quad (34)$$

and the specific flow through each pile by:

$$q_0 = \frac{Q_{pile}}{L} = \frac{Q_{tot}}{N_p * L} \quad (35)$$

Assuming that each pile is outfitted with a number of N_{sp} of slotted pipes, the specific flow within each pipe (q_{0pipe}) is calculated as:

$$q_{0pipe} = \frac{q_0}{N_{sp}} = \frac{Q_{tot}}{L * N_p * N_{sp}} \quad (36)$$

The required vacuum at the collection header is thus calculated according to equation (30) as:

$$P_w = \frac{\mu q_{0pipe}}{\pi k} \ln \left(\frac{R}{R_w} \right) = \frac{\mu}{\pi k} * \frac{Q_{tot}}{L * N_p * N_{sp}} * \ln \left(\frac{R}{R_w} \right) \quad (37)$$

Due to line losses between the collection header and the blower, due to equipment designed to protect the blower, the required vacuum at the blower is given by:

$$P_{blower} = P_w + P_{line} \quad (38)$$

where P_{line} represents the line vacuum loss, which is generally of the order of a few inches of water column.

Finally, the area necessary for the treatment unit (A), is calculated as:

$$A = L * [2N_p * R + (N_p - 1) * D] \quad (39)$$

where D represents the minimum distance between piles.

It should be noted that equation (38) can be solved for R or N_p if the treatment area is given.

Table 2 Design Conditions

Description	Symbol	Value	Units
Soil Volume	V	2000	m^3
Treatment Area	A	30×30	m^2
Minimum Distance Between Piles	D	1	m
Soil permeability	k	10^{-8}	cm^2
Soil Density	ρ	2000	kg/m^3
Treatment Time	T	90	days
Organics Concentration in Soil	C_o	1000	mg/kg

Equations (33), (34), (37), (38), and (39) relate all the parameters necessary for the design of a soil treatment system based on aeration piles, namely:

- number of piles necessary (N_p);
- the piles' dimensions (R and L);
- the number of slotted pipes per pile, and their radius (N_{sp} and Rw);
- the soil permeability (k);
- the treatment area; and
- the blowers' characteristics (Pw and Q).

An Example

This section utilizes the methodology developed in the previous section to provide the basis of design for treatment of a volume of soil based on the aeration pile technology. It is assumed that a treatment unit must be designed to remediate 2600 yd^3 , or 2000 m^3 of soil contaminated with 1000 mg/kg (1 g/Kg) of organics. The units must be contained within a $100' \times 100'$ area ($30 \text{ m} \times 30 \text{ m}$), and the aeration piles must be spaced at least 3 ft (1 m) apart. The permeability of the soil is 10^{-8} cm^2 , and the soil density is $2 \text{ kg}/\text{L} = 2000 \text{ kg}/\text{m}^3$. It is required that treatment be achieved over a three month (90 days) period. These conditions are summarized in Table 2.

The piles length is chosen to be 30 m, to fully utilize the available area. It is chosen to utilize a 4" slotted pipe, whose radius is 2", or 0.05 m. It is also chosen to construct a number $N_p = 4$ piles, each of volume 500 m^3 . The pile radius is then obtained by solving the following equation for R :

$$\frac{1}{2} \pi R^2 L = 500 \text{ m}^3 \quad (40)$$

where L was taken to be equal to 30 m. The resulting value of R is $R = 3.3 \text{ m} = 11 \text{ ft}$. The area required for construction of the units is calculated by use of equation (39), and is determined to be $A = 30 \text{ m} \times 29 \text{ m}$, so that the available area is sufficient for the treatment units.

The total flow required for aeration of the 2000 m^3 volume is calculated by use of equation (32), and is determined to be $Q_{\text{tot}} = 5.4 \times 10^6 \text{ L}_{\text{air}}/\text{day} = 5400 \text{ m}_{\text{air}}^3/\text{day}$, so that each pile needs to be aerated at a rate equal to $Q_{\text{pile}} = Q_{\text{tot}}/N_p = 1400 \text{ m}_{\text{air}}^3/\text{day} = 34 \text{ cfm}$.

It is chosen to install a number $N_{sp} = 4$ slotted pipes within each pile, so that the specific flow for each pipe is calculated via equation (36) to be equal to $q_{0 \text{ pipe}} = 11 \text{ m}_{\text{air}}^3/\text{m} \cdot \text{day}$. The required vacuum at the collection header is then calculated by use of equation (37) as $Pw = 2.6 \times 10^8 \text{ kg}/\text{m} \cdot \text{sec} \cdot \text{day} = 3100 \text{ kg}/\text{m} \cdot \text{sec}^2 = 12''$ water column. A knockout drum and a filter are installed between the collection header and the blower. It is

Table 3 Design Parameters

Description	Symbol	Value	Units
Length of Piles	L	30	m
Slotted Pipe Radius	Rw	2	inches
Radius of Piles	R	3.3	m
Number of Piles	N_p	4	
Number of Slotted Pipes per Pile	N_{sp}	4	
Total Air Flow	Q_{tot}	5400	$\text{m}_{\text{air}}^3/\text{day}$
Pile Air Flow	Q_{pile}	1400	$\text{m}_{\text{air}}^3/\text{day}$
Blower Vacuum	P_{blower}	30	iw c

estimated that these devices will produce a vacuum loss of approximately 18" of water column. The required pressure at the blower is then calculated as $P_{\text{blower}} = 12'' + 18'' = 30''$ water column. Thus, if a separate blower is installed for each soil pile, four blowers are able to produce 34 cfm at 30" water column vacuum will be required. If a single blower is manifolded to the four collection headers, it must be able to produce $34 * 4 = 136 \text{ cfm}$ at a 30" water column vacuum.

The design parameters, as determined by the above analysis are summarized in Table 3.

CONCLUSIONS

In this paper, we have presented a physical model describing the air flow induced by a slotted pipe held at a negative gauge pressure (vacuum) through a semi cylindrical soil pile. The coupled differential equations defining the model were solved numerically, and the influence of the main design parameters was examined. It was shown that, under normal operating conditions, the physical model's equation can be simplified, and turned into a set of equations useful for design purposes. An example of the use of the simplified equations for the design of the treatment units for a situation which might be encountered in practice was provided.

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PCB Cleanup Using an Oxygen/Fuel-Fired Mobile Incinerator

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A trial burn was recently conducted at a hazardous waste site containing soil contaminated with PCBs. Simulated soils containing 1 percent PCB and oils containing up to 40 percent PCBs were incinerated. The test results showed that >99.9999 percent of the PCBs were destroyed in a newly commissioned mobile incinerator incorporating an oxygen-fuel burner in the primary combustion chamber. In addition to the high destruction efficiency, particulates, HCl and CO were all well below the regulatory limits.

INTRODUCTION

Many industrial processes require substantial amounts of heat and energy produced by combusting hydrocarbon fuels such as natural gas, oil, or coal. Most of these processes use air as the oxidant. It is well known these processes can be enhanced by replacing some or all of the air with high purity oxygen (>90 percent) [1]. Partial replacement is known as oxygen enrichment while full replacement is known as oxygen-fuel or oxy-fuel for short. Oxy-fuel combustion technology has been successfully applied to the materials and minerals industries for many years, primarily for increased productivity and energy efficiency.

New developments have made oxy-fuel technology more attractive than ever before. In the past, the benefits of using oxygen could not always offset the added costs. New oxygen generation technologies, such as pressure and vacuum swing adsorption, have substantially reduced the energy requirements and therefore the cost to separate O₂ from air. This has drastically increased the number of applications where using oxygen to enhance performance is cost justified. Another important development is the increased emphasis on the environment. It has been shown that oxygen-fuel combustion can dramatically reduce NO_x and particulate emissions, which has also increased the number of cost effective applications [2]. The Gas Research Institute in Chicago, IL [3] and the U.S. Dept. of Energy [4]

sponsored independent studies which predict oxy-fuel combustion will be a critical technology in the very near future.

Incineration is a common method for destroying hazardous waste materials. Mobile waste incinerators have been designed for easy transportation and quick installation in remote locations where contaminated soils are typically located. It has recently been shown there are many benefits to using oxygen, instead of air, for combustion in these incinerators [5]. Typical improvements include higher destruction and removal efficiencies of the waste, increased thermal efficiency, increased processing rates, lower NO_x and particulates emissions, and less downtime for maintenance.

This paper discusses the general benefits of replacing air with oxygen in combustion processes along with its application to incineration and then presents the results of using oxygen in a trial burn for a soil remediation project using a newly constructed mobile waste incinerator.

OXY-FUEL COMBUSTION

Air consists of about 79 percent nitrogen and 21 percent oxygen by volume. Only the oxygen is needed in the combustion process. By eliminating nitrogen, many benefits are realized. They include increased productivity and energy efficiency with

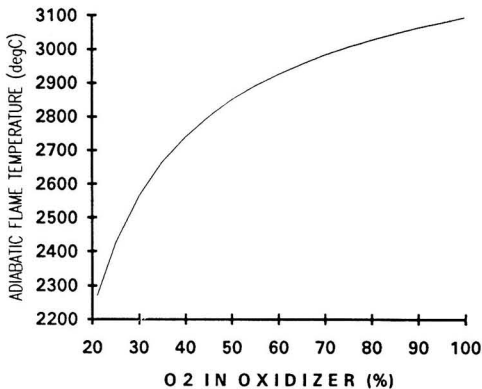


FIGURE 1. Adiabatic flame temperature for propane combusted stoichiometrically with oxygen and a variable quantity of nitrogen.

reduced flue gas volume and pollutant emissions. These benefits will be shown for the combustion of propane (C_3H_8) since this was the fuel used during the trial burn. However, the benefits are generally applicable to other fuels as well.

Increased Productivity

The flame temperature increases significantly when air is replaced with oxygen, i.e., as nitrogen which acts as a diluent is removed. Figure 1 shows the adiabatic equilibrium flame temperature for propane increases from 2300 to 3100°C when combusted with air and pure oxygen, respectively. In most furnaces and kilns, the dominant mode of heat transfer from the flame is radiation. Since radiation is dependent on the fourth power of the absolute temperature, the higher temperatures associated with oxygen increase the heat transfer to the load which increases the material processing rate. This means that more material can be processed in an existing system or that new systems can be made smaller for the same processing rate. This is particularly important in the portable incineration systems typically used in soil remediation since the size of the equipment is limited by what can be shipped over the road. Higher temperatures can also increase the destruction and removal efficiency (DRE) in waste incineration processes.

Increased Efficiency

Available heat is defined as the gross heating value of the fuel less the energy carried out of the process by the hot exhaust gases. Nitrogen in air acts as a ballast that carries energy out the exhaust. Figure 2 shows how the available heat increases with oxygen concentration in the oxidizer for a given exhaust gas temperature, in this case 1100°C. By using oxygen instead of air, more energy goes into the load instead of being wasted in heating up nitrogen. Since the energy needed to separate oxygen from air is only a small fraction of the energy used in the combustion process, the overall process saves energy. This also indirectly reduces the flue gas emissions since less fuel needs to be burned for a given production rate.

Reduced Flue Gas Volume and Particulate Emissions

Eliminating ballast nitrogen from air reduces the exhaust gas flow rate (see Figure 3). When the increased fuel efficiency is included, the flue gas volume can be reduced by over 80

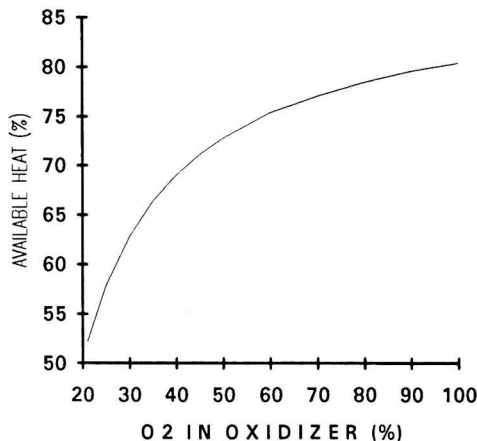


FIGURE 2. Available heat for propane combusted stoichiometrically with oxygen and a variable quantity of nitrogen at an exhaust gas temperature of 1100°C.

percent. This reduction makes it easier to treat the exhaust gases since the harmful emissions are in higher concentrations and therefore easier to remove. The size of the post treatment equipment can be proportionately reduced. The flue gas volume reduction has the added benefit of reducing the gas velocity by almost an order of magnitude. Lower gas velocities entrain fewer fine particles from the load which in turn reduces particulate emissions.

OXY-FUEL IN WASTE INCINERATION

Portable rotary kiln incineration systems are commonly used for remediating the soil at the contaminated site. In some cases, the decision to change from air to oxygen is influenced by the requirement to reduce the flue gas volume within the system for two reasons. First, the lower flue gas velocity in the kiln results in less particulate carryover to the secondary combustion chamber (SCC) and the air pollution control system. This reduces downtime and maintenance costs. Second, the flue gas residence time in the SCC is increased which typically increases the DRE.

At one Superfund cleanup site, oxy-fuel was selected to meet stringent particulate emission regulations set by the New Jersey

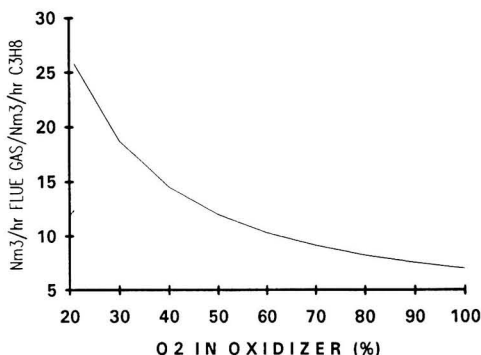


FIGURE 3. Normalized flue gas volume for propane combusted stoichiometrically with oxygen and a variable quantity of nitrogen.

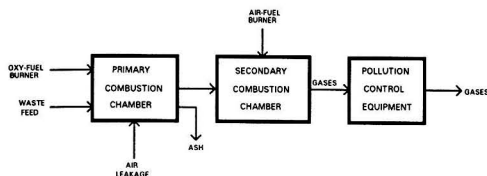


FIGURE 4. Waste incineration system block diagram.

Table 1 Trial Burn Input Parameters

Parameter	Units	Series		
		A	B	C
<i>Primary Combustion Chamber</i>				
Fuel	—	C ₃ H ₈	C ₃ H ₈	None
Oxidizer	—	O ₂	O ₂	None
Firing Rate	MW	0.79	0.79	0
Excess O ₂	%	15	15	N/A
Air Infiltration	kg/hr	1600	1600	1600
Soil Feed Rate	kg/hr	1375	1375	0
PCB in Soil	wt. %	1	1	N/A
Incoming Soil Temperature	°C	15	15	N/A
Incoming Soil Moisture	wt. %	8.9	8.9	N/A
<i>Secondary Combustion Chamber</i>				
Fuel	—	C ₃ H ₈	oil	oil
Oxidizer	—	air	air	air
Firing Rate	MW	2.3	2.5	3.0
Excess Air	%	10	10	10
PCB in Fuel Oil	wt. %	N/A	1	42

Department of Environmental Protection. Because the site was located near the coastline where the soil is naturally sandy, the existing regulations were cut in half to minimize the chance of any contaminated sand entering the atmosphere. Based on previous experience, the existing air-fuel system could not meet the stricter allowable emissions. Oxy-fuel combustion was selected to minimize particulate carryover by reducing the flue gas velocity to meet the new regulations. This became the first North American site to use oxygen-enhanced combustion in a commercial, transportable incinerator for the entire project. It was also the first Superfund site in the northeast region of the United States to use incineration. The average processing

rate increased 23 percent, the site was cleaned-up 60 days ahead of schedule, and all emissions and ash requirements were satisfied [6].

Vesta Technologies, Ltd. owns and operates portable waste incinerators that have been used at many hazardous waste sites around the U.S. and Canada over the last decade for soil remediation. Vesta found the performance of their incinerators could be enhanced by using oxygen instead of air in the primary combustion chamber. Baukal and Romano described how the performance of a typical Vesta incinerator was enhanced with oxygen [2]. At one site the average processing rate increased 150 percent, NO_x was reduced by two-thirds and the cleanup was completed one month ahead of schedule compared to previous data using air for combustion. This paper describes the results of a trial burn using a newly commissioned Vesta incinerator incorporating oxy-fuel.

TRIAL BURN RESULTS

Vesta conducted a trial burn for Hydro Quebec in Canada to destroy PCB-containing electrical transformers and related contaminated materials. The waste material is fed into one end of a rotary kiln. A single oxy-fuel burner located at the kiln entrance fires co-current with the feed material. The ash is collected at the kiln exit. The combustion and process off gases from the kiln are fed into the secondary chamber, which operates at a higher temperature than the primary chamber, to maximize destruction of any remaining combustible gases. A block diagram of the process is shown in Figure 4. The input parameters for the trial burn are listed in Table 1. Before the contaminated soil at the site was processed, the system was tested using surrogate wastes to ensure the emission requirements could be met. Three different series of tests were conducted using various combinations of fuels and wastes. An oxy-propane burner in the Primary Combustion Chamber (PCC) was used to incinerate PCB contaminated soil for series A and B. The only difference between A and B was that propane and oil with 1 percent PCB, respectively were used as fuels in the SCC. In series C, the PCC was not operated while the fuel for the SCC was oil with 42 percent PCB.

The trial burn results are listed in Table 2. The values for each series are the average of three sets of data taken on different days. The ash or cleaned soil exits the kiln and goes into a water bath which provides a seal for the kiln to minimize

Table 2 Trial Burn Results

Parameter	Units	Series			Regul. Limit
		A	B	C	
PCC Gas Temp.	°C	800	800	N/A	N/A
SCC Gas Temp.	°C	1230	1230	1230	N/A
Ash Temperature	°C	65	65	N/A	N/A
Ash Moisture	wt. %	30	30	N/A	N/A
PCB DRE	%	99.999972	99.999993	99.999996	99.9999
Combustion Efficiency	%	99.9929	99.9926	99.9976	99.9
Stack Particulate	mg/Nm ³	0.8377	3.320	2.556	50
Stack HCl	mg/Nm ³	N.D.	N.D.	N.D.	75
Stack CO	mg/Nm ³	9.95	10.6	7.4	114
Blowdown PCB	µg/l	N.D.	N.D.	N.D.	0.2
Blowdown 2,3,7,8 TCDD TE	ng/l	N.D.	N.D.	N.D.	0.12
Ash PCB	mg/kg	N.D.	N.D.	N.D.	0.5
Ash 2,3,7,8 TCDD	µg/kg	N.D.	N.D.	N.D.	1

N/A means not applicable.

N.D. means not detectable by instruments.

TCDD TE = tetrachlorodibenzodioxin toxic equivalent

air infiltration and also quenches the outgoing soil. The blow-down refers to the scrubber effluent.

All of the regulatory requirements were satisfied. In many cases the emissions were below the detectable limit of the instruments. Fewer particulates were generated when propane was the fuel in the SCC compared to oil. For series A and B, the PCC used about one quarter and the SCC three quarters of the total fuel input.

CONCLUSIONS

Oxygen was successfully used in the commissioning of a new mobile waste incinerator. At a hazardous waste site trial burn, PCB contaminants were efficiently destroyed using several configurations for waste feeds and fuels in both the primary and secondary combustion chambers. All measured pollutants were well within regulatory limits. Waste incineration is a promising application for oxy-fuel technology since throughput, energy efficiency, and DRE can be increased while simultaneously minimizing pollutant emissions and maintenance requirements.

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Final Disposal of VOCs from Industrial Wastewaters

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Vapor phase carbon adsorption followed by spent carbon regeneration and catalytic oxidation were evaluated as methods for disposal of volatile organic compounds (VOCs) released from industrial wastewaters during treatment operations such as aeration, air-stripping and aerobic biodegradation. Adsorptive capacities and breakthrough characteristics for eight VOCs found in many hazardous landfill leachates and contaminated groundwater were compared for selection of the best adsorbent and optimum treatment conditions. Coconut shell-based activated carbons exhibited higher VOC loading capacities than coal-based carbons, fiber carbon, molecular sieve and zeolite. Steam and hot nitrogen were both effective for regeneration of the spent carbon. A small quantity of adsorbates left in the regenerated carbon did not result in immediate VOC breakthrough in the next cycle adsorption treatment. Catalytic oxidation was found to be an attractive alternative for VOC disposal. Using a new commercial catalyst developed for destruction of halogenated organic compounds, even stable VOCs such as trichloroethylene and tetrachloroethylene were completely destroyed at < 350°C when oxidation was conducted at a space velocity of 17000/hr.

INTRODUCTION

Many industrial wastewaters, such as contaminated groundwater, manufacturing plant effluent, and hazardous landfill leachate, contain high concentrations of volatile organic compounds (VOCs) [1, 2]. VOCs released from wastewater treatment operations (aeration, air stripping, and aerobic

biodegradation) are a major source of air pollution [2, 3]. Finding an efficient and economical method for disposal of VOCs is often an important part of many industrial wastewater treatment projects. This paper presents a brief review of common VOC disposal methods and significant results of laboratory studies which were conducted for evaluation of two commonly employed disposal methods: vapor phase carbon adsorption followed by steam and hot nitrogen regeneration of spent carbon and catalytic oxidation.

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Table 1 Summary of Methods for Disposal of VOCs from Industrial Wastewaters

Disposal Method (%VOC removal)	Applicable Concentration (ppm _v)	Capacity Range (scfm)	Advantage	Disadvantage
Incineration (>99%)	100-2000	> 1000	complete destruction heat recovery possible wide applicability	high capital cost high operating cost VOC not recovered
Catalytic Oxidation (>95%)	5-2000	> 100	efficient destruction heat recovery possible lower fuel consumption	high capital cost uneven destruction catalyst poisoning VOC not recovered
Adsorption (60-99%)	< 5000	< 20000	VOC recovery low capital cost	need to regenerate carbon need to reduce humidity low removal efficiency for low b.p. VOCs
Condensation (50-95%)	> 5000	< 2000	VOC recovery low capital cost	low removal efficiency for low b.p. VOCs
Biofiltration (30-90%)	< 1000	< 1000	low capital cost low operating cost	limited applicability low removal efficiency variable performance

Selection of Processes for Disposal of Wastewater VOCs

Disposal of wastewater originated VOCs in a contaminated air stream can be accomplished directly by oxidative destruction or indirectly by separation which is then followed by thermal destruction or recovery. Oxidative destruction, which converts organic carbon to carbon dioxide, can be achieved by: incineration at a temperature > 1000°C; catalytic oxidation at < 500°C; or biofiltration at ambient temperature. Separation can be accomplished by condensation and adsorption. Applicability and relative advantages of these VOC disposal methods are summarized in Table 1 [3, 4]. Selection of the best disposal method is dependent on VOC characteristics (biodegradability, concentration, volatility, and water solubility), volume of the air stream to be treated, and the treatment cost. A separation/recovery method is preferred when a single VOC is present in high concentration, while a destruction method may be best for disposal of mixed VOCs [5, 6].

Figure 1 summarizes alternative treatment processes for removal of VOCs from industrial wastewaters. Liquid phase carbon adsorption is the simplest treatment scheme and is

useful when VOCs are present as minor contributors to total organic carbon (TOC) of the wastewater. The spent carbon is reactivated at a high temperature (> 900°C) by a regeneration vendor or on-site if the carbon consumption rate is high (> 5000 lb/day) [7]. Liquid phase carbon adsorption with in-situ steam regeneration is a logical choice when VOCs are main contributors to the wastewater TOC [8]. Several combinations of air or steam stripping with various separation and/or destruction methods are possible for treatment of VOC containing wastewaters. Additional treatment steps by biodegradation and/or liquid phase adsorption are necessary if removal of non-volatile TOC constituents is also required [9].

Efficiency of stripping depends on the Henry's Law constant of the organic compounds to be removed. The Henry's law constant for most compounds is roughly equal to vapor pressure divided by water solubility. Air stripping at a low air/liquid volumetric flow ratio (< 200) can remove from the wastewater feed VOCs with a high Henry's law constant (> 10⁻³ atm/g-mole), as a result of high vapor pressure (low boiling point) and low water solubility. Compounds with low Henry's law constants, however, required a much higher air/liquid ratio or steam stripping for effective VOC removal. Most often VOCs in air stripper exhaust are removed by vapor phase carbon adsorption. The vapor phase adsorbent may be used once for replacement or regenerated on-site for repeated use. Steam is the most commonly employed agent for regeneration. Hot nitrogen gas, however, is employed to desorb VOCs with high water solubilities which may react with steam or carbon in the adsorbent [10, 11]. VOCs on spent vapor phase adsorbent may also be desorbed by hot air and then destroyed by thermal oxidation or catalytic incineration [11, 12, 13].

Other more complicated VOC disposal processes may be justified for certain situations. A condensation and/or preheating unit is often included to reduce the relative humidity (RH) of contaminated air feed to the vapor phase carbon adsorbent to increase its capacity for VOCs [14]. A variety of heat recovery devices may also be included to reduce fuel cost for steam stripping, steam regeneration, or preheating the feed to incinerator or catalytic oxidizer [15, 16]. A vapor phase carbon adsorption and spent carbon regeneration system employing compression and expansion of nitrogen for heating and cooling requirements has been developed for recovering VOCs from a high flow air stream [17]. A hybrid system combining a rotary carbon concentrator/hot air regenerator unit with a fixed bed adsorbent/steam regeneration unit is effective for treating a high flow air stream with low concentrations of VOCs [18].

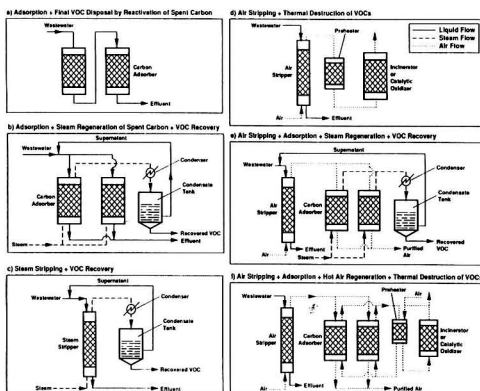


FIGURE 1. Processes for disposal of VOCs from Industrial wastewaters.

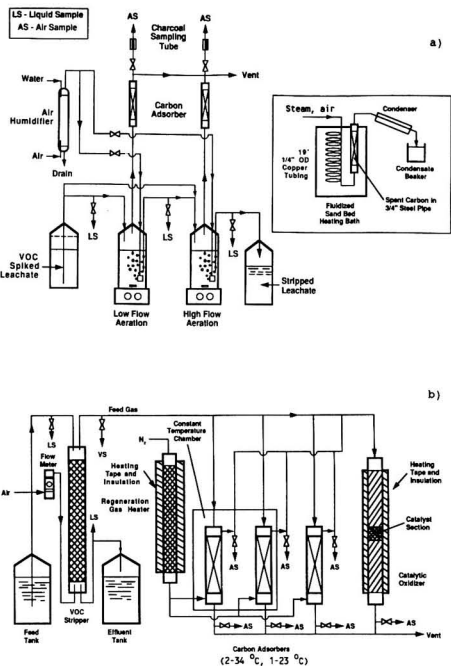


FIGURE 2. Experimental apparatus: a) aeration, carbon adsorption, and steam regeneration; b) air stripping, adsorption, desorption, and catalytic oxidation.

EXPERIMENTAL

Objectives

To assess the effects of important operating parameters for

key components of many VOC disposal processes such as air-stripping, vapor phase adsorption, spent carbon regeneration, and catalytic incineration, we have conducted extensive laboratory studies to: 1) determine the effectiveness of aeration and air stripping for removing VOCs from wastewater, 2) compare different adsorbents for VOC removal, 3) verify effect of humidity on capacities of activated carbon for mixed VOCs, 4) define carbon adsorption breakthrough profiles for mixed VOCs from air stripper exhaust, 5) obtain multi-cycle VOC loading and steam regeneration data, 6) obtain adsorption breakthrough and desorption profiles for mixed VOCs, and 7) evaluate catalytic incineration as an alternative VOC disposal method.

Experimental Procedures

A hazardous landfill leachate sample was initially employed in this study. The VOCs removed by aeration were adsorbed on a vapor phase carbon column which, after a period of adsorption service, was steam regenerated to obtain data for design of the VOC control section of the integrated leachate treatment system. In subsequent runs, an eight-compound cocktail (composition given in Table 2), which was prepared to simulate the VOC fraction of leachate TOC (2500 mg/L), was employed to spike the aerated leachate (67 ul/L) for repeated use as the wastewater feed. Aeration was conducted at two air/liquid flow ratios to simulate the aerated pretreatment (low aeration rate, 1 L/min in 3.5 L of spiked leachate in 4-L glass bottle) and the aerobic biodegradation (high aeration rate, 8 L/min) of the sequencing batch reactor (SBR) treatment of the leachate [9]. Before steam regeneration, the spent carbon column (a 3/4" diameter steel pipe) was preheated for ten minutes in a fluidized sand bed (FSB) heating bath. The bath was maintained at 200 to 300°C for heating the low pressure building steam and air which was provided to move the small amounts of steam employed for regeneration. Figure 2a illustrates the experimental apparatus employed for the aeration, vapor phase adsorption, and steam regeneration studies.

To ensure all VOCs were removed from the wastewater feed,

Table 2 Composition of VOC Cocktail, Aeration Tank Feed and Effluent

Compound	M.W.	B.P. (°C)	Density (g/ml)	Water Solubility (mg/L)	Henry's Law Const (atm-m ³ /mole)	Composition		
						Cocktail (ml/100 ml)	Feed ^{a,b} (mg/L)	Effluent (mg/L)
Methylene Chloride	84.9	40.1	1.335	16700	3.19×10^{-3}	4.5	(4) 3.0	0.3 ^c
Chloroform	119.4	61.2	1.485	9600	3.39×10^{-3}	25.4	1.8-4.3	0.1-0.4
							(25) 15	2.4
Trichloroethylene	131.4	86.7	1.459	1100	9.09×10^{-3}	6.2	(6) 2.3	0.2
							1.8-3.0	0.1-0.2
Tetrachloroethylene	165.8	121.0	1.625	150	28.70×10^{-3}	10.2	(11) 1.4	0.3
							0.7-1.6	0.2-0.3
Benzene	78.1	80.1	0.879	1830	5.55×10^{-3}	10.3	(6) 2.7	0.3
							2.6-2.9	0.2-0.7
Chlorobenzene	112.6	131.6	1.105	472	3.93×10^{-3}	5.5	(4) 2.5	0.5
							2.4-2.5	0.2-0.8
Toluene	92.1	110.7	0.866	535	5.93×10^{-3}	20.9	(12) 4.9	0.5
							4.5-5.2	0.2-1.3
O-Chlorotoluene	126.6	159.2	1.078	110	5.45×10^{-3}	16.8	(12) 3.4	0.7
							3.1-3.5	0.4-1.5

^aPreparation of test leachate sample (before spiking TOC=2500 mg/L):

- 1) acidified (pH 4.0), to prevent biological growth and minimize precipitation,
- 2) aerated for 30 minutes to provide a reference leachate without volatile organics,
- 3) spiked with 67 ul/L of organic cocktail,
- 4) fed to the aeration tank at 40 ml/min.

^bTheoretical concentrations based on the dilution of spiked cocktail are shown in parenthesis.

^cAverage of several measurements for the low aeration case (1 L/min), with ranges shown below.

Table 3 Moisture Uptake Data for Four Activated Carbons^a

Carbon Type	W _c	W _i	W ₀ 0 hr	W ₁ 2 hr	W ₂ 5 hr	W ₃ 8 hr	W ₄ 11 hr	% H ₂ O ^b
Calgon BPL	9.06	36.60	45.66	48.72	49.47	49.65	49.65	44.0
	9.35	36.42	45.77	48.90	49.65	49.85	49.85	43.6 43.8 ^c
Calgon PCB	8.20	35.86	44.06	47.10	47.35	47.50	47.61	43.3
	8.12	35.96	44.08	47.00	47.27	47.33	47.43	41.3 42.3
S-S 208C	8.55	37.51	46.06	48.94	49.66	49.78	49.90	44.9
	8.71	37.68	46.39	49.28	50.00	50.16	50.33	45.2 45.1
Ceca 46GE	9.60	36.85	46.45	49.54	50.22	50.27	50.27	39.8
	9.95	35.51	45.46	48.67	49.36	49.42	49.42	39.8 39.8

^aFlowrate of air for presaturation = 7 L/min; temp = 20°C

W_c = amount of dry carbon charged per adsorbed (g);

W_i = empty adsorber weight (g);

W₄ = water vapor saturated carbon adsorber weights (g).

^b% H₂O = (W₄ - W_i)/W_c.

^cAverage of the two runs.

a packed column air stripper was later employed in two series of multi-cycle studies (the first series VOC loading/steam regeneration runs: air flow = 8 L/min, liquid flow = 40 ml/L of tap water spiked 100 ul/L of the 8-VOC cocktail; and the second series adsorption breakthrough/nitrogen desorption runs: air flow = 4.2 L/min, liquid flow = 10 ml/min of tap water spiked with 0.3 ml/L of a 4-VOC cocktail). The column was also used in the catalytic oxidation runs, which employed the same air stripping as the adsorption/desorption runs. The VOC cocktails were first dissolved in ten volume of methanol to ensure fast dissolution of spiked VOCs in the tap water feed. Exhaust from the air stripper was nearly saturated with moisture, i.e., 100 percent RH. A constant temperature chamber was employed to conduct adsorption breakthrough experiments at 34°C to simulate treatment of 50 percent RH feed stream. The spiked tap water was used to simulate VOC containing groundwater which requires only air stripping for treatment.

Methylene chloride and chloroform broke through the carbon column very quickly while chlorobenzene and o-chlorotoluene (OCT) did not breakthrough long after others did, they were excluded in the four-VOC cocktail, consisting of 21.3 percent benzene, 14.4 percent trichloroethylene (TCE), 21.1 percent tetrachloroethylene (PCE), and 43.2 percent toluene, which was employed in the adsorption/desorption runs to facilitate monitoring of VOC breakthroughs. Heating tape and insulation were utilized to preheat nitrogen for VOC desorption and to provide elevated temperature for the catalytic oxidation runs. Figure 2b illustrates the experimental apparatus employed for air stripping, adsorption breakthrough, nitrogen desorption, and catalytic oxidation studies.

The pore size distribution of activated carbon depends mainly on the starting material. Coconut shell based activated carbons have predominantly small pores (diameter < 20 Å) and thus are mostly employed for vapor phase applications, such as air purification and solvent recovery. Bituminous coal based activated carbons typically have a bi-modal distribution of pore size, having large numbers of both small and larger pores (diameter 50–200 Å), and thus are particular suitable for liquid phase adsorption treatment for removing organic pollutant of all sizes [19]. Since coal based carbons are less costly, they are also employed in vapor phase adsorption, mostly for small disposable adsorbers containing 150 to 2000 lb of carbon. Two coconut shell based (Calgon PCB and Sutcliffe Speakman 208C), two bituminous coal based (Calgon BPL and Atochem Ceca 46GE) granular activated carbons, and two hydrophobic adsorbents (Union Carbide S-115 molecular sieve and Union

Carbide ELZ-10 zeolite) were compared for moisture uptake and adsorptive capacities for the VOCs. More than fifty total VOC loading (TVOCL) runs were performed to compare the four activated carbons abilities, both in as-received (dry) and moisture pre-saturated (wet) forms, in removing the eight VOCs found in the leachate. In addition, six cycles of VOC loading/steam regeneration runs were performed for two BPL adsorbers—one employing co-current regeneration and the other employing counter-current regeneration. For the counter-currently regenerated adsorber, an adsorption breakthrough time study was performed during the third cycle VOC loading run, and a sectional analysis was performed on the adsorber after the six cycle loading run. Calgon BPL and Calgon PCB were again compared in the six-cycle VOC breakthrough/nitrogen desorption runs. An activated carbon fiber adsorber was initially included in the comparative study; it was soon discontinued because of very low TVOCL and quick breakthrough of VOCs relative to adsorbents of the other two carbons.

Three monolithic catalysts—Allied Signal VOC (for destruction of hydrocarbon), HDC (for destruction of halogenated organic compounds), and THDC (HDC with improved tolerance for high temperature)—were tested in the catalytic oxidation at temperature from 200 to 500°C. A 1" × 7/8" diameter section (volume = 9.85 cm³) of catalyst was packed between two 8" × 7/8" diameter sections of ceramic honeycomb (the base material from which the catalysts were prepared

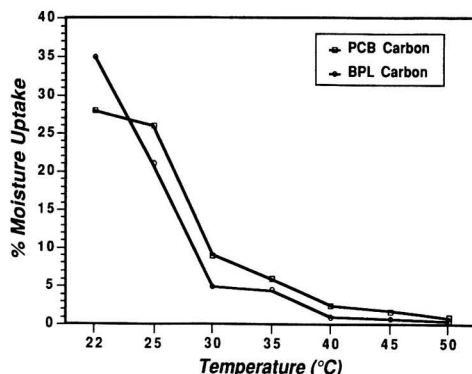


FIGURE 3. Moisture uptake on activated carbons (22°C 100% RH air feed; 9.8 g carbon, 1.4 L/min per adsorber, 24 hr).

Table 4 Summary of Total VOC Loading Runs

Column No.	Carbon Type	Wet/Dry ^a Carbon	Air ^b Flow Rate (L/min)	Run Time (hr)	TVOCL ^c	
					Inlet (mg/g)	Outlet (mg/g)
1	BPL	wet	1	11	172	48
2	BPL	wet	8	4.5	47	<1
3	PCB	wet	1	11	223	42
4	PCB	wet	8	4.5	56	<1
5	S-S 208C	wet	1	6	239	45
6	S-S 208C	wet	8	3	32	7
7	Ceca 46GE	wet	1	6	71	22
8	Ceca 46GE	wet	8	3	5	1
9	BPL	dry	1	14	206	58
10	BPL	dry	8	9	74	18
11	PCB	dry	1	14	221	59
12	PCB	dry	8	9	119	25
13	S-S 208C	dry	1	14	239	76
14	S-S 208C	dry	8	9	81	23
15	Ceca 46GE	dry	1	14	125	50
16	Ceca 46GE	dry	8	9	63	23

^aWet carbons were pre-saturated with moisture at 20°C, see Table 3.

^bAeration was conducted using experimental apparatus shown in Figure 2a.

^cBased on dry carbon; for specific compound loadings see Table 5.

by coating with specific precious metals), in a 2' glass column. The catalyst was replaced by an 1" section of the ceramic honeycomb in the control runs. At an air flow-rate of 0.7 to 2.8 L/min, the space velocity for the oxidation runs ranged from 4250 to 17000/hr. To assess the effect of RH on catalytic oxidation, a molecular sieve drying tube was employed to remove moisture from the feed stream.

VOCs in air samples were concentrated in 100 mg or 500 mg charcoal tubes (SKC, Inc.), and hexane was then utilized for extraction for analyses by GC using a flame ionization detector (Hewlett Packard Model 5880A). More than 90 percent recovery was achieved by single extraction using 10 ml of hexane for the 100 mg tubes; two or three serial ten ml hexane extractions were necessary to extract the 500 mg charcoal tubes employed in nitrogen desorption runs containing large quantities of VOC released from the carbon adsorber [20]. Solvent extraction was also performed on liquid samples at hexane/water, a volume ratio of 0.05 to 0.2; 70 to 95 percent recovery was noted for the liquid phase extraction. Concentrations of VOCs in the spiked tap water feed to the air stripper were also measured by GC employing direct injection of the feed samples. VOC concentrations, reported in mg/L for liquid samples and ppm, for air samples, were calculated from the GC area counts against a calibration curve prepared for each of the eight VOCs studied. To compensate for daily changes in GC sensitivity, at least one cocktail-in-hexane standard solution was included in each batch of GC measurements.

Specific experimental, sampling, and analysis conditions are given with the results presented in the tables and figures.

RESULTS AND DISCUSSION

VOC Removal by Aeration and Air Stripping

Table 2 presents important physical properties for the eight major VOCs found in the leachate sample as well as composition of the cocktail, spiked leachate, and aerated leachate. The measured VOC concentrations in the feed were all lower than the expected values calculated from the spiked amount. The reductions were due primarily to volatilization losses, as evidenced by higher losses for VOCs having higher Henry's Law constants, and less than 100 percent recovery for the hexane extraction of the feed samples. The low flow aeration (1 L/min), which simulated pretreatment of the leachate, removed at least 80 percent of VOC in the spiked leachate. More complete VOC removal (averaging 95 percent) was observed with the high flow aeration (8 L/min), which simulated aerobic biotreatment in SBRs. Nearly 100 percent removal for each VOC was achieved by air stripping employed for the multi-cycle adsorption/regeneration and catalytic oxidation runs.

Table 5 VOC Loadings on Four Activated Carbons^a

Compound	CALGON BPL		CALGON PCB		S-S 208C		CECA 46GE	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Methylene Chloride	0.16	0.67	<0.1	0.34	<0.1	0.76	<0.1	0.21
Chloroform	5.1	25.8	3.5	7.8	5.3	21.7	3.8	11.5
Trichloroethylene	3.4	11.6	2.2	3.6	3.2	10.3	2.1	5.1
Tetrachloroethylene	24.3	2.9	11.1	4.6	22.0	4.4	9.5	9.3
Benzene	2.2	14.9	2.3	4.9	2.2	13.5	2.0	6.7
Chlorobenzene	19.2	0.09	12.7	0.22	19.4	0.06	11.7	2.5
Toluene	25.1	2.0	19.2	3.7	23.5	2.9	15.0	13.8
O-Chlorotoluene	126	0.36	66.9	0.1	164	0.56	81.4	0.76

^aAmount of VOC adsorbed (mg/g carbon) for column numbers nos. 9, 12, 13 and 15, respectively. Experimental conditions are given in Table 4.

Table 8 Breakthrough Data for VOCs^a

Compound	Adsorption Loading Time ^b (min)													
	100	120	140	160	180	200	220	240	260	280	300	320	340	360
Methylene Chloride	0.42	0.82	1.5	1.7	1.4	1.2	0.96	1.2	0.84	0.82	0.91	0.85	0.77	0.63
Chloroform	0.06	0.37	1.6	4.9	6.2	7.8	7.9	7.0	5.0	4.7	5.4	4.9	4.5	3.8
Trichloroethylene	0	0	0.02	0.10	0.25	0.48	1.1	0.94	0.69	0.72	0.87	0.83	0.76	0.77
Tetrachloroethylene	0	0	0.03	0.03	0.06	0.12	0.35	0.32	0.23	0.32	0.44	0.45	0.44	0.61
Benzene	0	0	0.01	0.08	0.21	0.43	1.1	0.97	0.70	0.77	0.95	0.91	0.84	0.89
Chlorobenzene	0	0	0	0	0	0	0	0	0.01	0.01	0.01	0.01	0.01	0.03
Toluene	0	0	0	0	0.01	0.02	0.15	0.13	0.10	0.16	0.24	0.27	0.27	0.51
O-Chlorotoluene	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01

^aLoading (mg/g) on the 500 mg charcoal sampling tube; the charcoal tube was changed every 20 minutes. Spiked (100 ul/L) tapwater flow = 40 ml/min, air flow = 8 L/min.

^bVOCs were not detected in the adsorber effluent prior to 100 minutes.

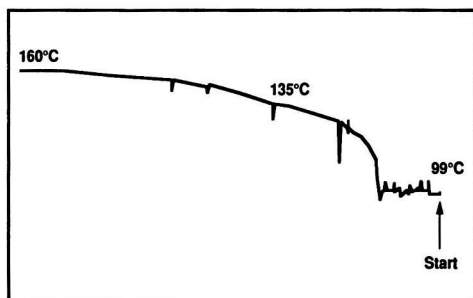


FIGURE 4. Temperature profile for adsorber effluent during steam regeneration (9.5 g BPL carbon with 4 g of moisture and 8 VOCs, FSB temp = 290°C, 10 min pre-heat, air flow = 3 L/min, 28 g steam supplied in 44 min).

quate for preparing spent carbon for the next cycle of adsorption treatment. Given the less than perfect analytical results (due to losses in sample handling, hexane extraction, and variable GC sensitivity) there were no significant declines in TVOCL and individual VOC loadings after five adsorption and regeneration cycles. Small quantities of VOCs remained on the regenerated carbon, especially in the inlet section where steam exited the adsorber, even with a high steam dose and a long regeneration time which provided a final effluent temperature of 160°C or higher (see Figure 4 for typical temperature rise during regeneration). As shown in adsorption breakthrough data (Table 8), such residual VOCs did not result in immediate breakthrough of any VOC. The order of VOCs found in the

adsorber effluent followed the order of increasing boiling point for these VOCs; methylene chloride (b.p. = 40°C) broke through after only 100 minutes, while OCT (b.p. = 159°C) did not breakthrough after 6 hours. The column breakthrough data also have demonstrated desorption of previously adsorbed low boiling point VOCs (methylene chloride, chloroform, TCE, and benzene), due to displacement by higher boiling point VOCs (PCE, chlorobenzene, toluene, and OCT). The loading data on adsorber sections (Table 9), which show lower loadings of less well adsorbed VOCs in the inlet section compared to other sections of the adsorber bed, have verified displacement of these compounds by more strongly adsorbed VOCs. As expected, immediate VOC breakthroughs were found in effluent samples of the adsorber which was regenerated by co-current steam.

Adsorption Breakthrough and Desorption Profiles for Mixed VOCs

Figure 5 shows that the coconut shell carbon (Calgon PCB) had more capacity for toluene (47 vs. 34 mg/g) than the coal based carbon (Calgon BPL). Also, the toluene capacity was reduced slightly (37 vs. 34 mg/g) after five cycles of adsorption and regeneration (by hot nitrogen). Figure 6 shows less reduction in TCE capacity (6.0 vs. 5.8 mg/g) as a result of five cycles of adsorption and regeneration operation. Figure 7 shows that small quantities of toluene and PCE remained in carbon long after the temperature for effluent nitrogen reached 150°C (toluene b.p. = 111°C and PCE b.p. = 121°C) while TCE (b.p. = 87°C) and benzene (b.p. = 80°C) were completely desorbed in less than half the time. Similar results were obtained for regeneration of the PCB adsorber using hot nitrogen (Figure 8). The desorption data also show that more toluene (52 vs. 38 mg/g) and TCE (7.8 vs. 4.5 mg/g) were released from the PCB adsorber than the BPL adsorber, consistent with the higher capacities of the shell based carbon observed during the loading run. Most residual toluene on the two adsorbers after the previous regeneration run must have been removed since the amounts released during the desorption runs were more than those adsorbed during the loading runs. This hypothesis is also supported by the loading data for the steam regenerated carbon (Table 7) which show no definitive increase in residual VOCs after five loading-regeneration cycles. Excellent VOC removal performance of a well designed and operated vapor phase carbon adsorption and steam regeneration system can be maintained for several hundred loading-regeneration cycles [24].

The enhanced capacity for VOCs due to feed gas preheating (from 23 to 34°C, RH reduced from 100 to 53 percent) were clearly demonstrated in Figure 9, in higher loading capacity for PCE (54 vs. 42 mg/g) and toluene (56 vs. 44 mg/g) and Figure 10, in delayed breakthrough for benzene and TCE. Again, the coconut shell based carbon performed better than

Table 9 VOC Loadings on Carbon Adsorber Sections^a

Compound	Adsorber Bed Depth ^b				
	inlet	25%	50%	75%	outlet
Methylene Chloride	0.09	0.11	0.06	0.11	0.16
Chloroform	2.4	3.5	3.9	3.9	6.1
Trichloroethylene	1.4	1.9	2.0	1.9	2.6
Tetrachloroethylene	5.4	5.5	4.5	3.4	3.2
Benzene	1.6	2.3	2.6	2.3	3.1
Chlorobenzene	6.8	3.7	1.6	1.3	0.54
Toluene	10.4	10.0	6.8	4.6	3.2
O-Chlorotoluene	39.8	6.1	1.9	2.5	0.62
TVOCL	67.9	33.1	23.3	19.9	19.5

^aVOC loading (mg/g) found in each section of the BPL column after the 6th cycle loading run; run conditions for the first 5 cycles are given in Table 7. Spiked (100 ul/L) tapwater flow = 40 ml/min, air flow = 8 L/min, adsorption loading time = 6 hours.

^b0.5 g carbon sample was taken from each section for loading analysis.

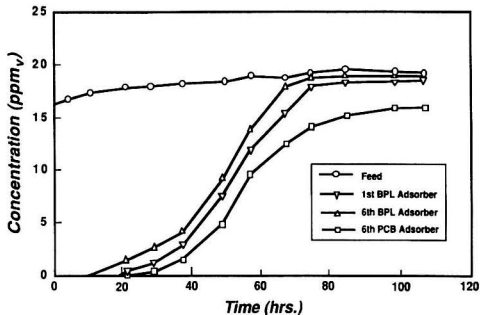


FIGURE 5. Adsorption breakthrough profiles for toluene—100 percent RH feed (air stripping at 20°C; 9.5 g carbon, 1.4 L/min per adsorber).

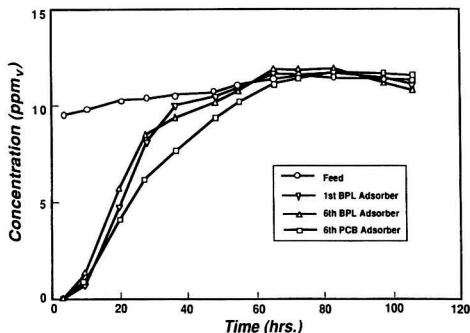


FIGURE 6. Adsorption breakthrough profiles for trichloroethylene—100 percent RH feed (air stripping at 20°C; 9.5 g carbon, 1.4 L/min per adsorber).

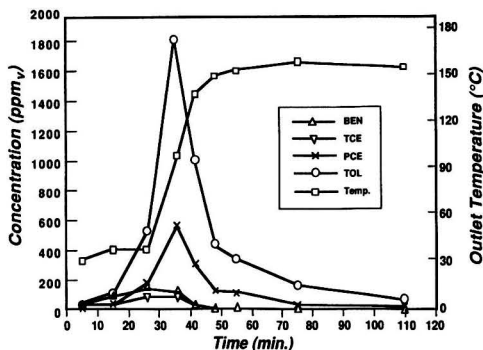


FIGURE 7. VOC desorption profiles—6th BPL adsorber (600°C nitrogen fed at 1.95 L/min).

the coal based carbon in the extended loading runs. Desorption of benzene and TCE was more significant in the pre-heated feed runs because more were loaded on the carbon adsorbers when the displacement phenomena occurred. Because of the potential for desorption of less well adsorbed VOCs in vapor phase adsorption for removal of mixed VOCs, the adsorber is frequently taken off from the treatment train for regeneration well before its full adsorptive capacity is utilized [11, 12, 14].

Catalytic Oxidation of VOCs

The catalytic oxidation data presented in Table 10 have shown that toluene was completely destroyed in all test systems

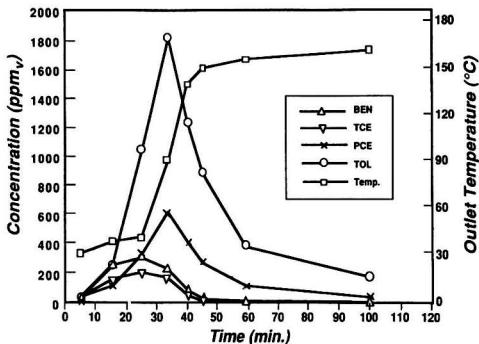


FIGURE 8. VOC desorption profiles—6th PCB adsorber (600°C nitrogen fed at 1.95 L/min).

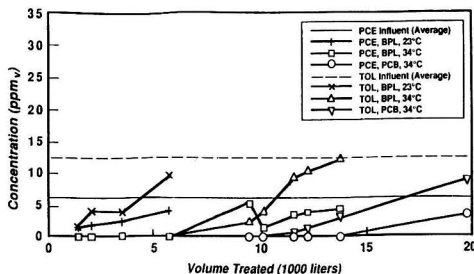


FIGURE 9. Adsorption breakthrough profiles for tetrachloroethylene and toluene (air stripping at 23°C; 9.5 g carbon, 1.4 L/min per adsorber).

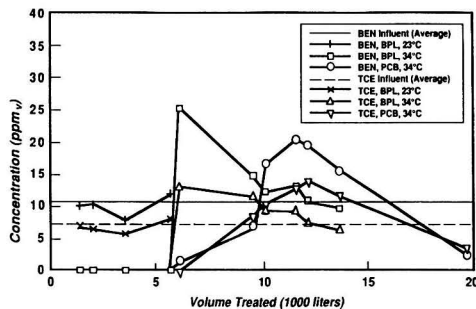


FIGURE 10. Adsorption breakthrough profiles for benzene and trichloroethylene (air stripping at 23°C; 9.5 g carbon, 1.4 L/min per adsorber).

at a temperature as low as 200°C and a space velocity of 17000/hr. At a space velocity of 8500/hr, benzene was also destroyed at 200°C, TCE was destroyed at 350°C, and PCE was destroyed at 500°C. The conventional hydrocarbon catalyst VOC was more efficient in destruction of benzene, while the special HDC and THDC were better for TCE and PCE, e.g., with the use of THDC, complete destruction of PCE was achieved at less than 350°C when oxidation took place at a space velocity of 17000/hr. Unlike vapor phase adsorption on activated carbon, about the same VOC destruction efficiencies were obtained when the humidity in the air feed stream was removed using a drying agent. The results have demonstrated that catalytic oxidation is an attractive alternative to the vapor phase adsorption and carbon regeneration process since it is a simple, low cost, one step treatment operation required for final disposal of VOCs [25]. The catalytic oxidation process should be even more attractive for disposal of VOCs when they are

Table 10 Summary of Catalytic Oxidation of VOC Runs

Catalysts: Allied Signal VOC control catalysts; Size: 1" × 7/8" dia. (9.85 cm³)
 VOC—for non-halogenated hydrocarbons, Lot No. PZM-13647.
 HDC—for halogenated VOCs, Lot No. PZM-13963.
 THDC—improved halogenated VOC catalyst, Lot No. PZM-14799.

Experimental runs: Oxidation of air stripping exhaust air
 Liquid feed: 10 ml/min of 4-VOC solution (0.3 ml of mixture^a in 20X methanol/L)

Catalyst Type	Sample	Oxidation Temperature (°C)	Space Velocity (1/hr)	BEN (ppm _v)	TCE (ppm _v)	PCE (ppm _v)	TOL (ppm _v)
No Catalyst (control)	Feed			28.0	15.0	12.0	25.0
	Effluent	350	8500	9.2	10.8	9.0	2.1
		350	4250	5.5	8.7	8.9	ND ^b
500		8500	3.6	7.3	8.7	ND	
VOC	Effluent	200	17000	2.4	7.1	10.3	ND
		200	8500	ND	5.8	9.5	ND
		350	8500	ND	ND	8.4	ND
		350	4250	ND	ND	7.8	ND
		500	8500	ND	ND	ND	ND
		500	17000	ND	ND	ND	ND
HDC	Effluent	200	17000	9.5	10.3	11.1	ND
		200	8500	3.8	7.9	8.3	ND
		200 (dry) ^c	8500	4.0	8.2	8.2	ND
		350	8500	ND	ND	5.5	ND
		350 (dry)	8500	ND	ND	2.0	ND
		350	4250	ND	ND	ND	ND
		350 (dry)	4250	ND	ND	1.1	ND
		500	8500	ND	ND	ND	ND
		500	17000	ND	ND	ND	ND
		500	17000	ND	ND	ND	ND
THDC	Effluent	200	8500	21.5	9.1	9.4	ND
		230	8500	17.6	8.1	8.4	ND
		275	8500	ND	ND	6.8	ND
		350	8500	ND	ND	ND	ND
		350 (dry)	17000	ND	ND	ND	ND

^aVolume fraction: BEN-0.213, TCE-0.144, PCE-0.211, and TOL-0.432.

^bLess than 0.5 ppm_v.

^cMoisture content of the feed reduced to <5%RH by passing thru a molecular sieve drying tube.

present in higher concentrations (up to 2000 ppm_v) in the feed stream, since more heat will be generated from oxidation which will reduce or even eliminate energy required for preheating [12].

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Application of Material Balance Concept in Waste Minimization Assessment of a Metal Finishing Process

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Microscale application of the material balance concept on a chrome-bearing metal finishing rinse tank was demonstrated to be a useful tool for evaluating waste minimization alternatives for plating rinses. Although more focused, the approach is easy to implement and once calibrated, the material balance model can predict process sensitivity for variables that are relevant to achieving waste minimization goals. In this case, substantial savings can be achieved in water usage and sludge generation by reducing flow-through rinse rates and installing mist spray rinses above concentrated finishing tanks.

INTRODUCTION

The metal finishing industry is subject to ever changing regulatory requirements, many of which affect ongoing business conditions of the industry. Two key issues in this regard are the increasing costs of operation, such as process chemicals and water, and the cost of complying with environmental regulations. Waste minimization is one way to reduce both of these costs.

Metal finishing wastes, specifically those derived from plating-type processes, are primarily liquid and solid, with the largest volume contributed from flow-through, post-finishing, aqueous rinse tanks. These wastewaters contain process drag-out, the film of solution clinging to metal parts as they are removed from plating baths. Hazardous substances in rinse wastewaters include toxic heavy metals and, in some cases, cyanides. The quantity of rinse water may range from 1 gpm (3.8 l/min) per rinse tank in a job shop to 6–8 gpm (23–30 l/

min) per tank for industrial finishing. A large facility with several metal finishing lines, therefore, may generate in excess of 150,000 gal/day (568 m³/day) of hazardous wastewater [1]. Rinse tanks are also replaced frequently (e.g., daily or weekly) and concentrated baths very infrequently (once every one to three years or longer), contribute additional metal-laden discharge. Pretreatment of metal finishing wastewaters is most commonly accomplished by chemical precipitation resulting in the generation of sizable quantities of heavy metal sludges which must be disposed of offsite as hazardous waste (e.g., F006). Options that reduce wastewater and/or sludge quantities generated while maintaining product quality often offer the greatest potential for waste minimization.

Literature describing source reduction and waste minimization efforts in metal finishing industries is abundant. Projects ranging from general improvements in housekeeping and maintenance to complex process changes requiring extensive facility modifications are addressed. A substantial number of

publications present methods and case studies for reducing drag-out losses, reducing rinse contamination and volume, and reducing discharges of hazardous materials through structural and/or operational changes in plating bath and aqueous rinsing processes [1-9]. However, few of these studies have been generated in the context of a rational methodology that goes beyond site specificity, and at the same time is focused enough to obtain engineering data to support expected waste reductions and evaluate waste minimization alternatives. This paper presents an example of an attempt to evaluate and achieve reductions in rinse-waste usage and sludge generation in a metal finishing process in the context of a waste minimization assessment.

Waste Minimization Assessments

The principal tool for initiating waste minimization activities at individual facilities is the waste minimization site assessment. Waste minimization manuals have been published by the U.S. Environmental Protection Agency and various states as a guide to generators and inspectors for conducting site assessments leading to a waste minimization plan at individual facilities [9-12]. The site assessment or data collection component of the methodology outlined in these manuals receives the most attention since this information not only provides an engineering basis for waste minimization assessment and design, but also establishes a baseline for accurate determination of achievements in waste reduction and cost effectiveness once a specific design has been put in place. Interestingly, although published assessment manuals typically contain numerous, itemized, process data sheets and sections for detailed process flow diagrams and material balances, the use of such tools is conspicuously absent from virtually all of the case studies reported in the literature. The apparent reasons for this shortfall are: the difficulty of obtaining such detailed information at a site since the required data are not routinely recorded at the facility, and waste minimization assessments typically take only a large-scale, overall view of a facility which limits the ability to engage in the more focused approach required to carry out material balance analyses for individual plant processes. While this latter effort is important for identifying priority waste streams, the site assessment should proceed to a second stage of more detailed data collection and analysis. In this paper, we demonstrate the use of chemical data and a simple material balance model to analyze and evaluate waste minimization alternatives for a priority metal finishing waste stream at the Texas Instruments—Dallas Manufacturing site (TI-DM).

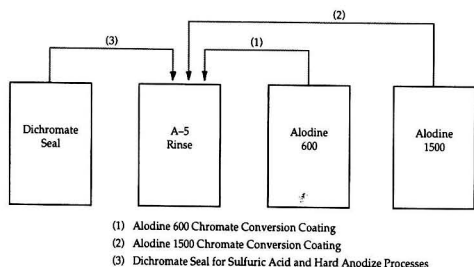


FIGURE 1. Line A finishing processes involving Rinse Tank A-5.

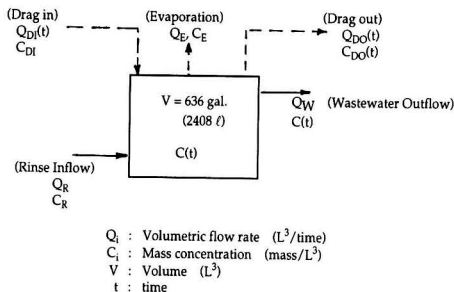


FIGURE 2. Conceptual material balance for Rinse Tank A-5.

CONCEPTUAL DEVELOPMENT

The chemical finishing shop at TI-DM consists of three major finishing lines which operate two, 8-hour shifts daily. Two of these, Lines A and B, feature chrome finishing of aluminum and steel parts, respectively. The process chosen for focused study was a key rinse tank from Line A, designated as tank A-5 (see Figure 1). Tank A-5 is an immediate rinse for four different finishing processes involving chromate coatings: 1) Alodine 600 Chromate Conversion Coating; 2) Alodine 1500 Chromate Conversion Coating; 3) Sulfuric Acid Anodize Coating which includes a Dichromate Seal; and 4) Hard Anodize Coating which also includes a Dichromate Seal. The relevant portion of the four process sequences involving rinse tank A-5 is noted in Figure 1.

The selection of rinse tank A-5 was predicted on several factors. A preliminary waste minimization assessment of metal finishing operations at the plant identified chromium wastewater treatment and sludge disposal as the most costly waste-related undertaking at the facility. Virtually all chromium wastewater derives from the rinse tanks in the various finishing lines. Furthermore, Line A is the busiest of the finishing lines at the plant, and rinse tank A-5 is the primary rinse for three of the four concentrated chromium tanks in the line. Thus, although it is more difficult to model, it is certainly representative of chromium rinsing operations at the facility, and waste minimization achievements therein can be conservatively extrapolated to other chromium rinses in the plant.

Tank A-5 is a single flow-through rinse operated at 90°F (32°C). A relatively high flow-through rate and aeration combine to achieve a high degree of mixing. Figure 2 shows the various inputs and outputs to A-5 that serve as the basis for formulation of a material balance on total chromium (Cr), which at this stage is 87-97 percent hexavalent and the remainder in the reduced trivalent state. The nonsteady state mass balance expression is of the general form:

$$\left[\begin{array}{c} \text{Accumulation of Cr} \\ \text{in tank} \\ \text{per unit time} \end{array} \right] = \left[\begin{array}{c} \text{Mass flow of Cr} \\ \text{into tank} \\ \text{per unit time} \end{array} \right] - \left[\begin{array}{c} \text{Mass flow of Cr} \\ \text{out of tank} \\ \text{per unit time} \end{array} \right] \pm \left[\begin{array}{c} \text{Gain or loss of Cr} \\ \text{due to reaction} \\ \text{within tank} \end{array} \right]$$

Using the symbols from Figure 2 and assuming negligible reaction of total chromium in the rinse tank, the material balance on total Cr for A-5 is:

$$V \frac{dC(t)}{dt} = Q_R C_R + Q_{DI}(t) C_{DI}(t) - Q_W C(t) - Q_{DO}(t) C(t) - Q_E C_E \quad (1)$$

where

V = volume of rinse tank (L³)
 C = chromium concentration (M/L³)
 Q = volumetric flow rate (L³/t)
 t = time

and subscripts,

R = rinse inflow
 DI = drag-in
 W = waste outflow
 DO = drag-out
 E = evaporation

The Cr concentration in the inflow rinse is assumed to be zero, thus dropping this term out of equation 1. Drag-in flow rate and concentration can be averaged over an 8-hour shift and thereby treated as having constant values over the time period or, preferably, handled as time-variable inputs using the work log to estimate their distributions. Laboratory tests conducted at 90°F (32°C) enabled estimation of the evaporation rate, Q_E , as approximately 3 percent of the inflow rate which matched well with measured/metered values of Q_W and Q_R . Evaporation water, however, was assumed to be relatively Cr-free, zeroing this term. The exit flow rate, Q_W , is simply $Q_R - Q_E$ and is 6 gal/min (22.7 l/min), while the concentration is $C(t)$, the time-variable, completely mixed flow concentration in the tank. The drag-out concentration is also $C(t)$, while the flow rate, $Q_{DO}(t)$ can be handled similarly to the drag-in rate. As will be seen, setting $Q_{DO}(t) = Q_{DI}(t)$ provides a more than adequate estimate for this input term. The lefthand side or accumulation term is simply the tank volume times the time

rate of change of concentration in the tank. Equation 1 is easily rearranged to:

$$\frac{dC(t)}{dt} + \frac{[Q_{DO}(t) + Q_W]}{V} C(t) = \frac{Q_{DI}(t) C_{DI}(t)}{V} \quad (2)$$

the solution of which is:

$$C(t) = \frac{b}{a} (1 - e^{-at}) \quad (3)$$

where:

$$a = \frac{Q_{DO}(t) + Q_W}{V} \quad (4)$$

and:

$$b = \frac{Q_{DI}(t) C_{DI}(t)}{V} \quad (5)$$

In order to more easily accommodate time-variable drag-in flows and concentrations, a numerical solution to equation 2 was developed using a fourth-order Runge-Kutta algorithm.

RESULTS AND DISCUSSION

Test Cases

Test data are reported for two days that are considered to be representative of the work load at the facility. Hourly samples were collected from the tank A-5 outlet for chromium analysis using an ISCO 2700 autosampler. This gives the value $C(t)$ in equations 2 and 3. Grab samples were collected from the concentrated Alodine 600, Alodine 1500, and dichromate seal tanks, also for chromium analysis. These enabled estimation of drag-in concentrations, $C_{DI}(t)$. Total chromium was measured according to EPA Method SWA 46-7190 using a Varian Spectra 400 Atomic Adsorption Spectrophotometer.

Rinse inflow, outflow, and evaporation rates were determined as noted previously. The most difficult model inputs to acquire are the drag-in and drag-out flow rates. Visual inspection enables estimation of drag-in volume for a single pass, although this will obviously vary based upon the shape, number, and stacking of parts in a particular job. Dwell time over the finishing tanks is sufficient to effect substantial drainage before passing into the rinse. Estimates of Q_{DI} were on the order of one liter for the Alodine 600 and Dichromate Seal tanks which are adjacent to Rinse A-5, and about 25 percent less than this value for passes from the Alodine 1500 tank which have to travel a greater distance. As is evident from equation 4, the drag-out flow rate, Q_{DO} , is small compared to Q_W (typically less than 0.3 percent) and thereby has a negligible effect on the solution. Thus, as noted previously, Q_{DO} was simply set equal to Q_{DI} .

In Test Case 1, data were obtained for the first shift only. The two shifts are fairly well balanced in terms of the work load with the first shift occasionally more active than the second. On this day, there were two Alodine 600 jobs, three Alodine 1500 jobs, and six Dichromate Seal jobs over the initial 8-hour period. Table 1 gives the load schedule for one-hour intervals for the full 16-hour work day using information from the work log. Also included are the resulting drag-in flow rates and concentrations averaged over the interval using the following mass balance:

Table 1 Time-Variable Drag-In Flows and Concentrations for Test Case 1 Based Upon Work Log and Model Calibration

Hour	Jobs	Q_{DI} (l/hr)	C_{DI} (mg/l)*
First Shift			
1	(1) Alodine 600 (1) Alodine 1500 (2) Dichromate Seal	3.19	3019.1
2	(1) Alodine 1500 (1) Dichromate Seal	1.49	2462.4
3	-0-	-0-	—
4	(1) Dichromate Seal	0.85	4021.3
5	(1) Alodine 600	0.85	2991.2
6	-0-	-0-	—
7	(1) Alodine 1500 (1) Dichromate Seal	1.49	2462.4
8	(1) Dichromate Seal	0.85	4021.3
Second Shift			
9	(1) Alodine 600	0.85	2991.2
10	(2) Alodine 600	1.70	2991.2
11	(1) Alodine 600	0.85	2991.2
12	(1) Alodine 600	0.85	2991.2
13	(1) Alodine 600	0.85	2991.2
14	-0-	-0-	—
15	(2) Dichromate Seal	1.70	4021.3
16	(2) Dichromate Seal	1.70	4021.3

*Total Chromium

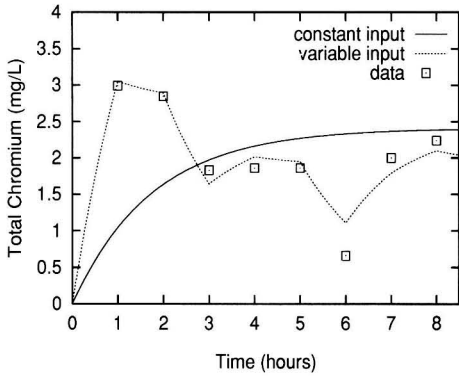


FIGURE 3. Rinse A-5 chromium concentration: Test Case 2 data and model simulations for time-variable versus constant rate of input.

$$C_{DI}(t) = \frac{\sum_j [Q_{DI,j}(t)C_{DI,j}(t)]}{\sum_j Q_{DI,j}(t)} \quad (6)$$

Note that the ordering and timing of runs is estimated based on the work log and may not be precisely as given in Table 1. Data and a model calibration for Test Case 1 are shown in Figure 3. For this case, the concentration at time zero is assumed to be zero since the tank was washed out following preceding use. The dashed line in Figure 3 represents the total chromium concentration in Rinse Tank A-5, $C(t)$, as simulated by the Runge-Kutta solution of equation 2. The simulation was fitted to the data by adjusting the drag-in volume per pass from the original estimates by a constant percentage from all tanks. The calibration exercise resulted in values that were 85 percent (to the nearest 5 percent) of the initial estimates, or 0.85 liters per pass of Alodine 600 and Dichromate Seal runs and 0.64 liters per pass for Alodine 1500. Although drag-in volumes will likely vary slightly from job to job, it is evident that the model calculations follow the trends in the experimental data quite well. For comparison, Figure 3 also includes the analytical solution of equation 3 for 8-hour averaged values of Q_{DI} and C_{DI} .

Figure 4 depicts data and model simulations for two shifts (16 hours) of a second test case. Unlike Case 1, the tank was not cleaned following the previous day's work. An initial sample revealed a rather high (8.0 ppm) concentration of chromium which was used to start the numerical solution. The same values for drag-in flows from Case 1 were used in the Case 2 simulations and the work log used to determine the job order which is summarized in Table 2. Once again the simple material balance model tracks the measured concentrations of total chromium in the rinse tank outlet rather well when time-variable drag-in flows and concentrations are used. The most notable deviations are at extreme high and low points such as at 2, 4, and 7 hours. This result also lends verification to estimates of the drag-in flows obtained from the calibration exercise for Test Case 1.

Implications for Waste Minimization

Once calibrated and verified, the rinse tank model can be used to perform sensitivity analyses that predict the response of the reactor to various process changes. Of particular interest in the waste minimization problem are: 1) the impact of reducing the flow-through rate of rinse water in the tank, and

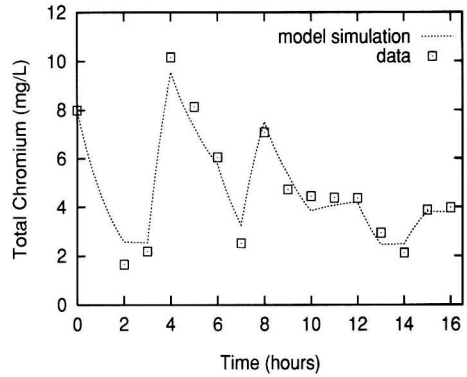


FIGURE 4. Rinse A-5 chromium concentration: Test Case 2 data and model simulation using drag-in flows from Case 1.

2) the impact of changes in the drag-in flow and/or concentration. Examples of sensitivity analyses for these variables are illustrated in Figures 5 and 6. Both figures were constructed using inputs from Case 2.

Figure 5 demonstrates the impact on rinse tank chromium concentration of reducing the influent rinse rate from the current level of just over 6 gal/min (22.7 l/min). For this "typical" work day, the chromium concentration rises to a maximum of over 11 mg/l for a flow reduction of 2 gal/min (7.6 l/min). Presently, the chemical finishing shop contributes about 60 percent of the chrome rinse flow to wastewater treatment, the remainder deriving from the plating laboratory and lab sinks. Given current data on the composite chromium concentration entering the chromium wastewater treatment unit, a 2 gal/min (7.6 l/min) reduction across all chrome rinse tanks in the chem-

Table 2 Time-Variable Drag-In Flows and Concentrations for Test Case 2 Based Upon Work Log and Case 1 Calibration

Hour	Jobs	Q_{DI} (l/hr)	C_{DI} (mg/l)
First Shift			
1	-0-	-0-	---
2	-0-	-0-	---
3	(1) Dichromate Seal	0.85	4021.3
4	(2) Alodine 600	6.80	3763.8
5	(6) Dichromate Seal		
	(1) Alodine 600	1.70	3506.3
	(1) Dichromate Seal		
6	(2) Alodine 600	1.70	2991.2
7	-0-	-0-	---
8	(3) Alodine 600	5.10	3506.3
	(3) Dichromate Seal		
Second Shift			
9	(1) Dichromate Seal	0.85	4021.3
10	(1) Alodine 600	0.85	2991.3
11	(1) Alodine 600	1.70	3506.3
	(1) Dichromate Seal		
12	(1) Alodine 1500	1.49	2462.4
	(1) Dichromate Seal		
13	(1) Alodine 1500	0.64	383.8
14	(1) Dichromate Seal	0.85	4021.3
15	(3) Alodine 600	2.55	2991.2
16	(2) Alodine 600	1.70	2991.2

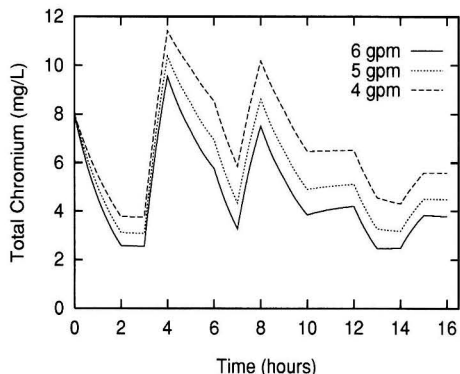


FIGURE 5. Sensitivity of chromium concentration in Rinse A-5 to flow-through rinse rate using Case 2 variables.

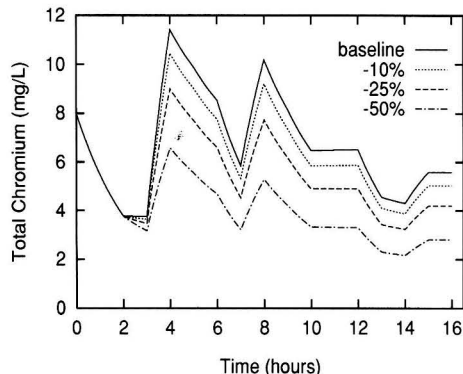


FIGURE 6. Sensitivity of chromium concentration in Rinse A-5 to percent reductions in drag-in achieved by process tank spray rinsing (Case 2 variables).

ical finishing shop would raise the composite wastewater influent concentration to between 5.0 and 6.0 mg/l. This value is still well within the range of treatment effectiveness of the chrome wastewater treatment system for achieving discharge standards, while affording the potential for substantial savings in water use and sludge generation and disposal. The possible drawback to this course of action, however, is a decrease in product quality due to increased chrome residual and resulting in a larger percentage of rejections. A common solution to this problem is modification of the rinsing system to incorporate several countercurrent rinses operating in series. Space limitations at the TI-DM facility, however, prohibit such modification for this rinse tank.

An alternative in this case is to install mist spray rinses above the concentrated chrome tanks. This would not require additional water usage as spray rates could be calculated to approximate the make-up water required to counter evaporation losses in the concentration tanks which are operated at elevated temperatures. More importantly, spray rinses would reduce the mass of chromium transported to the rinse tank per pass via drag-in, ensuring achievement of satisfactory product quality. Figure 6 illustrates the potential impact of pre-rinse spraying on rinse tank performance. The baseline curve in Figure 6 is a model simulation using Case 2 inputs and a reduced flow-through rinse rate of about 4 gal/min (15.1 l/min). Subsequent curves represent simulations for respective percent reductions in the mass per unit time of chromium entering the rinse tank as drag-in, given by the right-hand side of equation 2. A reduction of just 25 percent brings chromium concentrations within the range of current values. Product literature on spray rinses over process tanks does not provide expected percent reductions in mass per unit time of metal in the drag-out. Given: 1) the operating temperature and evaporation rates of the process tanks, 2) the average number of passes per unit time through individual process tanks, and, 3) the fact that drag-out volume per pass is greater than drag-in volume due to the relatively lengthy trip of product bins from surface preparation steps to process tanks, it is likely that total spray rinse volumes for a single pass will be at least as great as the drag-out volume, promoting at least a 1:1 dilution of chromium in the drag-out. It is not unreasonable, therefore, to anticipate mass reductions to the rinse tank of up to 50 percent, allowing for reduction of the flow-through rinse stream to as low as 4 gal/min (15.1 l/min) without appreciable degeneration in product quality.

Cost Recovery

A reduction of 2 gal/min (7.6 l/min) for the rinse tank flow rate results in an annual water and wastewater savings of over

one-half million gallons, assuming 275 operating days per year. If the same percent reductions are extended to all chrome rinse units in the chemical finishing shop, the savings come to approximately 7.5 million gallons per year or 24 percent of chromium rinse waters generated. This translates into a projected savings of approximately \$32,500 per year in water, sewer, and treatment costs. The wastewater volume reduction combined with maintaining rinse waste chromium concentrations at current levels by using pre-rinse sprayers will produce an additional \$32,500 per year in sludge disposal costs for a total of \$65,000 per year in savings. This amount will provide near-term recovery of the cost of installing mist sprayers over the concentrated chromium tanks. Similar analyses could be performed for the other finishing lines to achieve potential additional savings.

In addition to assessing waste minimization alternatives, the calibrated model simulations such as those presented in Figures 5 and 6 can be used to schedule work so as to avoid chromium spikes in the tank as depicted between hours 3 and 5 and hours 7 and 9. The model can also be used to anticipate influent loading to the treatment plant without having to apply continuous monitoring.

SUMMARY

Detailed analysis of the performance of a flow-through, chrome finishing rinse tank demonstrated that a simple material balance model could adequately simulate the time-concentration profile of chromium leaving the tank. Calibration of the model with actual chemical data was also demonstrated to be a useful means of obtaining more accurate estimates of drag-in flows. Once calibrated, the model was then used to evaluate various waste minimization options focusing on savings in water use and wastewater and treatment sludge generation. In this particular case, savings of up to \$65,000 per year can be achieved for the chrome finishing operation alone by a combination of reducing flow-through rinse tank rates and installing mist sprayers above the concentrated chrome tanks. The focused approach illustrated in this exercise can be applied to many other industrial processes as a useful tool in conducting waste minimization assessments.

ACKNOWLEDGMENTS

The authors thank Mr. David Moore of Texas Instruments—Dallas Manufacturing for assisting us in data collection.

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Remediation of a VOC-Contaminated Superfund Site Using Soil Vapor Extraction, Groundwater Extraction, and Treatment: A Case Study

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A case history of remedial action taken at the primary contaminant source area within the Verona Well Field Superfund Site in Battle Creek, Michigan. Included is a site description, a description of the soil and groundwater treatment systems, plus a summary of the lessons learned through six years of active remediation.

INTRODUCTION

In the early 1980s, a Thomas Solvent Company facility was found to be the primary source of groundwater contamination at the Verona Well Field Superfund site in Michigan. Facility operations and leaking underground storage tanks (USTs) resulted in subsurface soil and groundwater contamination including a 1.2-meter- (4-foot-) thick floating nonaqueous phase liquid (NAPL) layer. The primary contaminants are benzene, toluene, xylene, tetrachloroethene (PCE), trichloroethene (TCE), and their breakdown products.

A combined remediation approach of groundwater extraction and soil vapor extraction (SVE) was implemented at the 0.4 hectare (1 acre) site beginning in 1987. To date, the groundwater extraction system has removed more than 6,400 kg (14,000 pounds) of priority pollutant contaminants. The groundwater is treated in a nearby air stripper. The SVE system removed more than 20,500 kg (45,000 pounds) of priority pollutants before being shut off in June 1992. A groundwater sparging system was implemented in late 1991 to aid in the remediation of the capillary zone soils near the groundwater interface. Both vapor-phase carbon and catalytic oxidation were used to treat SVE system offgas.

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While the identified program has proven to be highly effective for site remediation—unsaturated soils have met the site remediation objectives (less than 14 ug/kg PCE)—many lessons have been learned during the course of system implementation and operation. These include:

- use care when applying site characterization data to design
- understand the site conceptual model before starting remediation and update the site conceptual model, as necessary, during remediation
- consider all the regulations that will apply to the remedial action
- be flexible in selecting and implementing treatment technologies
- evaluate more than just the key contaminants (look at the big picture)
- plan effective, inclusive coordination with all relevant federal, state and local agencies
- do not underestimate the importance of effective public relations.

The knowledge gained in carrying out this site program can and should be applied to other sites undergoing remediation. Benefits will include a reduction in cost and frustration.

BACKGROUND

The Verona Well Field (Figure 1) provides potable water to approximately 50,000 residents in and around Battle Creek, Michigan. In August 1981, volatile organic compound (VOC) contamination was detected in approximately one-third of the City's production wells and in numerous private wells in the vicinity of the well field. Initial investigations of the site by the EPA identified three potential sources of the contamination and a contaminant plume with VOC-concentrations of up to 346 $\mu\text{g}/\text{l}$ in the well field. The three source areas are also identified on Figure 1.

A solvent distribution facility run by the Thomas Solvent Company was found to be the most contaminated of the source areas. This facility, referred to as Thomas Solvent Raymond Road or TSRR, was used for the storage, transfer, and packaging of chlorinated and nonchlorinated solvents from the mid-1960s until 1984. Contamination of the soil and groundwater at TSRR is thought to have resulted from underground tank leakage and surface spills in the tank truck loading/unloading areas. Leak tests completed in 1984 found 9 of the 21 underground tanks on the site to be leaking. Vadose zone contamination covered more than 0.4 hectare (1 acre), and a 1.2 meter (4-foot) thick floating NAPL layer was identified under a portion of the site.

EPA signed a Record of Decision (ROD) in the fall of 1985 to address the contamination at the TSRR facility. The ROD specified a corrective action that included a network of groundwater extraction wells to remove the contaminated groundwater, the treatment of extracted groundwater by air stripping, and a soil vapor extraction (SVE) system to remove VOCs from the unsaturated zone soils.

SITE CHARACTERISTICS

The TSRR facility covers approximately 0.4 hectares (1 acre). The site is located in the bottom of a wide river valley. Site topography is flat. The lithology of the site consists of fine to coarse grained sand with traces of silt, clay, and pebbles. The water table is approximately 6.1 meters (20 feet) below grade and the hydraulic gradient is towards the well field in the northwesterly direction. The hydraulic conductivity is on the order of 10^{-2} to 10^{-3} cm/sec.

SITE REMEDIATION SUMMARY

Site remediation was initiated in 1986 with the demolition of most site structures and the general grading of the site. The 21 USTs could not be removed from the site at that time due to the high concentration of VOCs in the subsurface soils; any excavation at the site would have results in a violation of Michigan air regulations.

Groundwater extraction was initiated early 1987, and is ongoing today. Soil vapor extraction was implemented in the spring of 1988. The SVE system operated until the fall of 1990, when the system was shut down due to a change in EPA contracts. The USTs were removed from the site in early 1991, and the SVE system was reconstructed and operated until June 1992. Groundwater sparging was pilot tested in mid-1991 and then operated full scale from December 1991 through May 1992.

Soil samples collected in June 1992 indicate that the vadose (unsaturated) soils meet the Michigan cleanup requirements. However, the groundwater and capillary zone soils still exceed the respective clean up goals. The need for further action to address the capillary zone soils is currently being decided.

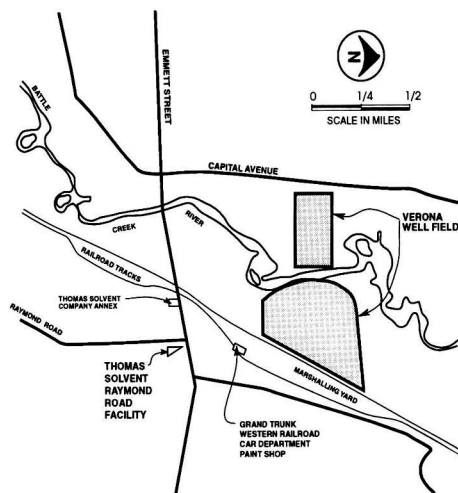


FIGURE 1. Vicinity map.

Groundwater Extraction

The installation of nine groundwater extraction wells at the TSRR facility began in the fall of 1986, and the groundwater extraction system began operating in March 1987. The wells are 200 mm (8-inch) diameter carbon steel and are screened from approximately 6.1 to 10.7 meters (20 to 35 feet) below grade. One of the wells was constructed as a dual extraction well for the recovery of the floating NAPL. The extracted groundwater is pumped from the submersible well pumps to a monitoring building onsite where the water discharges into a common header and then flows via gravity to an air stripper located in the well field for treatment. The treated water is discharged to the Battle Creek River.

Since start up, more than 6,400 kg (14,000 pounds) of VOCs have been extracted with the groundwater. Groundwater concentrations, once as high as 19,000 $\mu\text{g}/\text{l}$ total VOCs, have decreased to 500 $\mu\text{g}/\text{l}$ total VOCs. The NAPL layer was removed in the first year and a half of operation with approximately 550 liters (150 gallons) of NAPL recovered through dual extraction. The groundwater extraction system continues to operate with 8 wells and a combined extraction rate of approximately 1325 liters per minute (350 gpm). Total VOC concentrations in groundwater downgradient from the site and outside the contaminated zone have decreased by 50 percent since system start up through natural attenuation.

Soil Vapor Extraction

Design and construction of the SVE system began in November 1987 with operation of a pilot test to determine fullscale design parameters. Full scale operation of the SVE system began in March 1988. The SVE system included 23 vapor extraction wells, an air/water separator, offgas treatment equipment, and two system blowers. Figure 2 presents a simplified schematic of the system. The site layout is presented in Figure 3.

The vapor extraction wells are constructed out of 50- and 100-mm (2- and 4-inch) PVC pipe. Slotted well screens extend from approximately 1.5 meters (5 feet) below grade to 0.9 meters (3 feet) below the water table. Each well has a throttling valve, sample port, and a vacuum gauge. The wells were connected by means of an above ground surface manifold. The

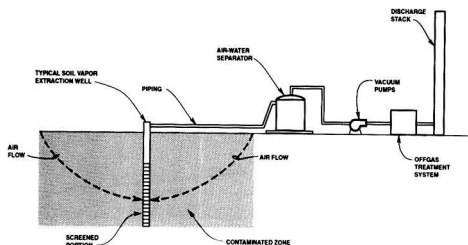


FIGURE 2. Schematic of soil vapor extraction system.

manifold is connected to the air/water separator, which in turn is connected to the blowers and offgas treatment system.

The SVE system operated from March 1988 through September 1990, and following tank removal from March 1991 through June 1992. Operation was generally limited to less than 14 wells at a time with well head concentrations determining the wells selected for operation. This was done to maximize contaminant loading to the offgas treatment system. Extraction rates from the SVE wells were typically $2.8 \text{ m}^3/\text{min}$ (100 scfm), with the combined flow between 34 and $45 \text{ m}^3/\text{min}$ (1,200 and 1,600 scfm). Wellhead vacuums in the extraction wells were typically 50 to 80 mm (2 to 3 inches) of mercury.

During the course of operation, the SVE system removed approximately 20,500 kg (45,000 pounds) of VOCs from the site vadose zone. The total VOC loading rate dropped from an initial high of approximately 490 kg (1,080 pounds) of VOCs removed per day to under 0.5 kg (1 pound) per day.

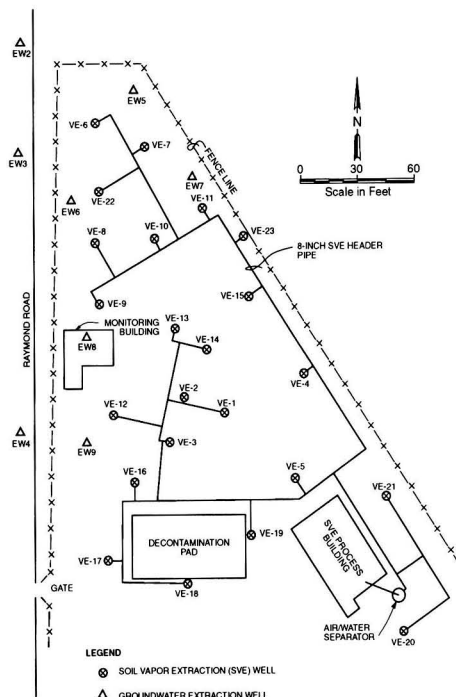


FIGURE 3. Soil vapor extraction system.

Offgas Treatment

Offgas from the SVE system was initially treated using vapor-phase activated carbon adsorption to remove the contaminants from the vapor stream. That system was replaced in January 1990 with a catalytic oxidation unit. Activated carbon was again used from March 1991 through June 1992.

The carbon adsorption system consisted of two sets of four stainless steel carbon vessels connected in series. The primary set of vessels was used for the majority of VOC adsorption, while the second set acted as backup in the event of breakthrough from the primary vessels. Each vessel held approximately 450 kg (1,000 pounds) of vapor-phase carbon. During system operation, an in-line organic vapor analyzer between the primary and secondary carbon units was used to monitor contaminant breakthrough. When breakthrough occurred, the primary carbon was sent offsite for regeneration, and the secondary carbon placed in the primary position. During system operation, approximately 123,000 kg (270,000 pounds) of carbon were loaded with VOCs and shipped offsite for regeneration. The average carbon loading during the project was 16 percent.

The catalytic oxidation system is essentially a thermal reactor designed to destroy vapor-phase chlorinated and nonchlorinated VOCs onsite. A schematic of the system is presented in Figure 4. The SVE extraction stream flows from the blowers through a heat exchanger, into the burner, across the catalyst bed where destruction of the VOCs occurs, back through the heat exchanger and out a discharge stack. The products of combustion are carbon dioxide, water vapor and hydrochloric acid. The system is capable of greater than 99 percent destruction/removal efficiency (DRE) for VOCs. The catalytic oxidation system was operated at the TSRR site for approximately one year without any operating difficulties or decrease in destruction efficiency.

Groundwater Sparging

Groundwater sparging is a developing technology designed to focus remedial efforts on the capillary zone just above the water table. In a typical sparging system the sparging gas, usually compressed air, is injected into the subsurface below the water table. The sparged gas then moved up through the saturated zone and into the unsaturated zone due to buoyant forces, providing gas-phase movement and contaminant release points in typically stagnant zones.

At the TSRR site, a groundwater sparging system using nitrogen as the sparging gas was pilot tested and then implemented full scale in mid-1991 to address residual NAPL contamination in the capillary zone soils. Soil sampling and analysis completed in February 1991 indicated that the majority of the soils at the site met the cleanup objectives, but the capillary zone soils in the area where the NAPL had previously been identified did not. Following an assessment of available treat-

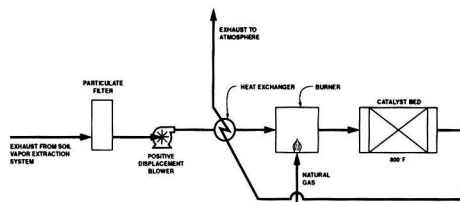


FIGURE 4. Schematic of catalytic oxidation system with heat recovery.

ment options, sparging was identified as an emerging technology that may be able to address the residual contamination.

The full scale sparging system had three 50 mm (2-inch) diameter sparging wells screened from 3 to 3.7 meters (10 to 12 feet) below the water table. Nitrogen was generated onsite through a membrane process generator that was able to supply the gas to the wells at the desired injection rate and pressure. Injection pressures of approximately 260 mm Hg (5 psi) were used to sparge the nitrogen gas at an injection rate of approximately 0.4 m³/min (15 cfm) per well. Nitrogen was used as the sparging gas because of the high reduced iron content in the groundwater.

The full scale sparging system operated from December 1991 through May 1992. During that time groundwater concentrations decreased by more than an order of magnitude (from 1,500 µg/l TVOCs to less than 150 µg/l), and soil gas concentrations initially increased and then stabilized at near pre-sparging levels. In the months following sparging, a gradual increase in contaminant concentrations in the groundwater was observed until groundwater concentrations again reached pre-sparging levels.

LESSONS LEARNED DURING REMEDIATION

By and large, the TSRR remediation project has been a success. To date, the public water supply has been stabilized, the contaminant source areas identified and addressed, and soil and groundwater contamination at the primary source area reduced to the point where the unsaturated soils meet the predetermined cleanup objectives. However, that is not to say that the remediation has proceeded without learning a number of important lessons that should be applied to future remedial actions at other sites. The particular lessons learned in the course of this project that are discussed in this paper include:

- use care when applying site characterization data to design
- understand the site conceptual model before you start remediation, and update the site conceptual model, as necessary, during remediation
- consider all the regulations that will apply to the remedial action
- be flexible in selecting and implementing treatment technologies
- evaluate more than just the key contaminants (look at the big picture)
- plan effective, inclusive coordination with all affected federal, state and local agencies
- do not underestimate the importance of effective public relations

Use Care When Applying Site Characterization Data to Design

Site characterization data for the TSRR site estimated the total VOC contaminant mass in the vadose soil at 1350 kg (3,000 pounds). This estimate was made based on soil sampling and analysis data, and was used in the sizing of the SVE and offgas treatment systems. About 1350 kg (3,000 pounds) of VOCs were then removed during the 70 hour SVE pilot tests, and in total, over 20,500 kg (45,000 pounds) of VOCs have been removed from the vadose soils since start up.

The lesson here is to know where the site data comes from and what it actually means. Accepting data without question or qualification can be costly and dangerous. If you are not sure about the quality of your data, limit its use and collect more data as necessary. It is also important to consider using environmental scientists and geostatisticians to help guide proper data interpretation and assess quantitative variability. It is the engineer's job to design within the uncertainty defined

by the scientist and statistician. However, designs, at least in the environmental arena, are often completed without a proper analysis of the data's basis and uncertainty.

Understand and Update the Site Conceptual Model

Before the start of the remediation, the site data suggested that there was an approximately 0.4 hectares (1 acre) area of contaminated soil and groundwater to contain in order to prevent further offsite migration of contaminants. There was also reported to be a floating NAPL pool in the center of this area. The NAPL was to be recovered in a dual extraction well while the onsite plume was contained with eight additional wells. What was not known until beginning the remediation was that the NAPL layer was up to 1.2 meters (4 feet) thick in one well. This required a reevaluation of the operational strategy during startup.

After close to three years of SVE operation, the offgas concentrations had decreased substantially to less than 0.5 kg (1 pound) of VOCs removed per day. At the same time however, soil boring sample results indicated that the vadose zone soils within 0.6 to 1 meters (2 to 3 feet) of the water table still exceeded the cleanup criteria for several compounds. Field studies indicated that there was good air flow in the capillary zone, but contaminant removal had reached a plateau. Through the evaluation of past and present data and the results of several NAPL column studies, the problem was defined as one related to the residual NAPL in the capillary zone. The remainder of our soil remediation efforts were then focused on this target zone.

Do not get stuck with an outdated model of the site. Conditions will change due to natural forces and the results of the remediation. Validate the initial assumptions and reevaluate the site conceptual model throughout the remediation process. Adjust the remediation systems as appropriate. Site remediation is a dynamic process, and using an observational approach to remediation is essential in order to constantly narrow the focus of the remediation. The cycle of collecting data, adjusting the site model, modifying the designing, implementing the change, and collecting more data should be maintained throughout the project.

Consider All the Regulations That Will Apply to the Remedial Action

The 0.4 hectare (1 acre) TSRR site contained 21 USTs and an above ground loading dock/solvent transfer building. The soil was so contaminated that there was no practical way to excavate the USTs without violating the Michigan air regulations, so the groundwater and soil remediation had to proceed with the tanks still in the ground. The tanks weren't removed until three years after the SVE system began operating. This complicated the cleanup effort, but the remediation was completed without violating the air regulations.

The lesson here is that there are many regulations that can affect the design, construction, startup, and operation of a treatment plant on a hazardous waste site. It can be extremely costly not to know what those regulations are, and how and where they apply. At the same time, knowing the regulations can often help identify cost savings, or least cost alternatives. In either case, it is generally worthwhile to have a regulatory specialist on the project team.

Be Flexible in Selecting and Implementing Treatment Technologies

Just over a year after starting up the SVE system using carbon for offgas treatment, catalytic oxidation became com-

mercially available as an offgas treatment alternative. A cost benefit analysis identified a cost savings to the project as long as the offgas contaminant loading remained above the calculated break-even point. With that information in hand, the EPA was able to approve the change, and the catalytic oxidation system was installed a short time later.

About a year after the catalytic system was implemented, the project team began looking for a way to address residual NAPL in the capillary zone just above the water table. After completing a literature search and several soil column leaching studies, it was decided to pilot test air injection and groundwater sparging [1]. Groundwater sparging proved to be the most effective, and several months later it was implemented full scale at the site.

Both of these changes were important to project execution. It wouldn't have been as easy to make these changes without a flexible contract with the EPA that allowed for system optimization, or if either change had required a ROD amendment. In both cases the EPA worked with CH2M HILL to implement the best solution for the site. It is important to have flexibility with regards to the treatment system. This is especially true in order to be able to take advantage of new technologies or technological changes as they develop. It is also true with regards to changing site conditions and concentrations. Remediation projects typically take at least several years. During the project period, new technologies will undoubtedly emerge that should be considered.

Evaluate More Than Just the Key Contaminants— Look at the Big Picture

Shortly after the groundwater extraction system went online, the pump efficiencies started to decrease dramatically. Upon investigating the problem, the project team found that the well screens were being blocked by iron bacteria. Iron bacteria are aerobic bacteria that need a source of oxygen and a source of reduced iron to thrive, and both had been provided in the extraction wells. To combat the iron bacteria in the wells, a twice monthly chlorination program was initiated.

The dissolved iron problem manifested itself in other ways too. Within several years, piping from the wet well to the air stripper became blocked by iron bacteria deposits. This caused pumps to burn up and valves to fail. Because of iron depositing in the air stripper, the packing had to be replaced four years after beginning the groundwater extraction program at TSRR.

Even if the high dissolved iron levels in the shallow groundwater and the presence of iron bacteria in the aquifer had been known, the project team may not have done anything differently with regards to the design of our extraction and treatment system. But the operational problems could have been anticipated and prepared for. Instituting a chlorination program from start up might have resulted in more efficient operation. In designing the treatment system, all of the primary contaminants that exceeded the groundwater cleanup criteria had been planned for, but the levels of other compounds like dissolved iron or the presence of iron or sulfur bacteria were not fully considered. The lesson learned is that water samples need to be analyzed for all compounds that could potentially affect the design and operation of the treatment system.

Plan Effective, Inclusive Coordination With All Affected Federal State and Local Agencies

Several years after the contaminants in the City's well field were identified, all of the agencies involved in the remediation project—the Department of Public Health, the Department of Natural Resources, the EPA, the City Water Department, and the USGS—realized that the project could be more effective

if everybody worked together. Although the different parties had informally communicated as needed before this time, everyone began sharing documents, gathering input on different aspects of the remediation, and meeting as a group two or three times a year to bring everyone involved from the different regulatory agencies up to date and to present a forum for voicing concerns and ideas. These meetings often involved 20 or more people and lasted the entire day, but the change in project execution was dramatic. Suddenly each agency knew what the others were doing, and everybody worked together to provide the most effective and efficient means of addressing site concerns.

Similarly, when in the planning stages for removing the USTs, the project team sought the involvement of county officials and the local fire department. This was important because they would know what was going on at the site and would have concerns regarding the safety of the project team and the safety of the local residents. By the time the tank removal took place, the local officials and fire department were familiar with the plans and comfortable with the safety precautions.

The point is that as a general rule, there are many people and agencies that will have a say or at least an opinion in any remediation project. You can either work together or you can work apart. Our lesson was that the project went much more smoothly when everyone worked together.

Do Not Underestimate the Importance of Effective Public Relations

The Verona Well Field remediation project started with poor and often disjointed public relations. The affected population close to the site were told different things by different agencies, or, in some cases, not told anything at all about the situation. This resulted in the complete distrust of the agencies involved by the local residents. To some extent this feeling continues today. Rather than being the "good guys" who were addressing the remediation problem, the project team and government agencies involved were often looked upon as dishonest and mistrustful.

With some success, the public's image of the project team was changed by holding public availability sessions where people were able to meet with the project team in small groups or on a one-to-one basis. This format prevents a small vocal opposition from dominating and disrupting the meeting. It also provides a good forum for addressing and discussing the concerns of individual citizens. Public meetings don't provide the same atmosphere because the podium separates the speakers from the public, and a few hostile people can control the meeting. Only in meeting the concerned citizens on their terms in small groups was the project team able to effectively convey the findings and plans the remedial action.

Keeping the affected public informed is extremely important in effectively carrying out a remediation project because if you do not they can and will hold protests, write letters to the media and elected officials, and generally try to disrupt your actions regardless of your intent.

SUMMARY

While all of these lessons may not be new to every reader, they were new or important to the project team at the time, and they have been incorporated into subsequent projects. Many of the lessons are also applicable to other environmental restoration projects that are addressing the same issues and in some cases, learning the same lessons.

ACKNOWLEDGMENTS

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CO₂ Capture from the Flue Gas of Conventional Fossil-Fuel-Fired Power Plants

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Research has been conducted at Argonne National Laboratory to identify and evaluate the advantages and deficiencies of several technologies, both commercially available and alternative technologies, for capturing CO₂ from the flue gas of utility boilers that use air as an oxidant (the current universal practice). The technologies include chemical solvent, cryogenic, membrane, physical absorption, and physical adsorption methods. In general, technologies for capturing CO₂ are expensive and energy-intensive. Therefore, they result in a substantial overall increase in the cost of power generation. Research to improve the performance and economics of these technologies is discussed.

INTRODUCTION

Methods for avoiding emission of CO₂ to the atmosphere are receiving increasing attention because CO₂ emissions are expected to contribute to future climate change via the greenhouse effect. This paper reviews several technologies that can (or promise to) capture CO₂ from the flue gases of today's fossil-fuel-fired utility boilers. These technologies have reached their present state of development for reasons other than avoiding climate change. Indeed, they were developed for several reasons: acid-gas cleanup, CO₂ capture for enhanced oil recovery, and CO₂ capture for use in the beverage industry. Now it is appropriate to ask if these technologies might be put to a related but different use—avoiding CO₂ emissions.

To further that inquiry, estimates are given of the amount of CO₂ emitted by power plants, and various methods of CO₂ capture are described. These methods are chemical solvent, physical absorption, cryogenic, membrane, and physical adsorption.

Several topics pertinent to avoiding emissions of CO₂ and other greenhouse gases, including CH₄ and N₂O, have been addressed elsewhere [1, 2, 3] and are not discussed here. Strategies for controlling CO₂ emissions, other than CO₂ recovery from conventional flue gas, are also discussed elsewhere [4]. These strategies include: (a) combustion of fuels in oxygen, yielding a mixture that is primarily H₂O and CO₂ from which water can be easily separated [5], and (b) partial (or total) elimination of carbon from fuels before combustion [6].

CO₂ EMISSIONS

Amount of CO₂ Emited from Power Plants

Data on electric power generation by fossil-fuel-fired power plants in the United States are compiled by the Energy Information Administration (EIA) [7]. We used these data to estimate the thermal efficiencies at which the power was generated from various fossil fuels and to estimate the quantities of CO₂ generated by fossil-fueled power plants, using the following assumptions and approximations:

1. Chemical composition of the hydrocarbon content of coal is assumed to be CH_{0.8}.
2. Chemical composition of petroleum is assumed to be CH_{1.39}, and its density is assumed to be 849 kg/m³ (53 lb/ft³).
3. Heating values of the different fossil fuels used for power generation were taken to be the averages reported by EIA for July 1991 [7]:
Coal —23,870 kJ/kg (20,525,135 Btu/ton). This implies that about 60 percent of the coal mass is represented by the formula CH_{0.8}.
Petroleum —6.6 × 10⁶ kJ/bbl (6,313,470 Btu/bbl).
Natural Gas—38,174 kJ/m³ (1,025,250 Btu/1000 ft³).
4. Power production from September through December 1991 was estimated relative to production in 1989 by using the same ratio for the first eight months of the two years.

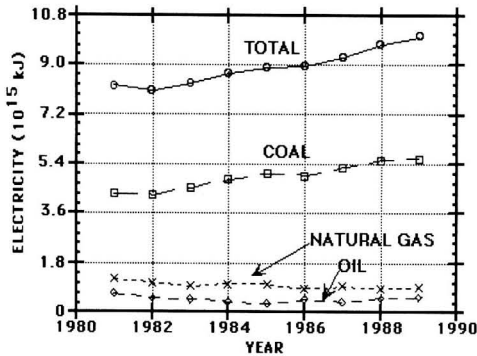


FIGURE 1. Power production in the United States during the 1980s using different fuels.

The results were found later to be in good agreement with the data published by EIA [8].

Figure 1 shows the total electric power (fossil, hydro, and nuclear) produced in the United States over the last decade and the amounts produced by coal, petroleum, and natural gas. The data indicate that over 50 percent of the electric power was generated using coal. While generation using natural gas and petroleum fuels did not increase in the 1980s, generation using coal increased by over 20 percent during the same period. This is significant because, of the three fossil fuels considered, coal generates the most CO₂ per unit of fuel energy. Figure 2 shows approximate material and energy balances for a typical coal processed by a conventional coal-fired power plant. This figure shows that a conventional coal-fired power plant produces over 0.25 gram of CO₂ for each kilojoule of electrical energy (or 0.9 tonne/MWh). The generation of CO₂ also liberates about 80 percent of the coal energy (the other 20 percent comes from burning the H₂ in the coal).

Figure 3 shows the power generation efficiencies attained in the 1980s. Coal-fired plants are more efficient than either petroleum- or natural-gas-fired facilities, primarily because many of the oil- and natural-gas-fired plants are older, and consequently less efficient, units that are used only for meeting peak demands. Properly designed natural-gas-fired base-load units should be able to achieve higher efficiencies. Furthermore, as natural gas is mostly CH₄, over 50 percent of the energy of combustion of natural gas comes from its H₂ content, while H₂ provides only about 20 percent of the energy of combustion for coal. Therefore, a significant reduction in CO₂ emissions can be realized if coal is replaced with natural gas. However, CH₄ is itself a greenhouse gas that, mole for mole, is suspected to contribute between 10 and 30 times more to the greenhouse effect than does CO₂ [1, 2]. Thus, comparison of coal with natural gas must take CH₄ leaks into account.

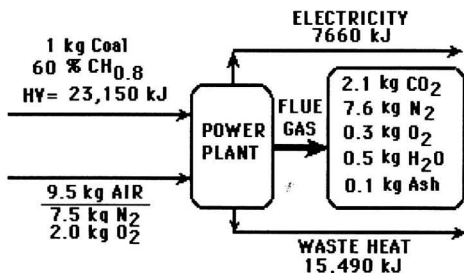


FIGURE 2. Products of coal combustion with 110 percent theoretical air.

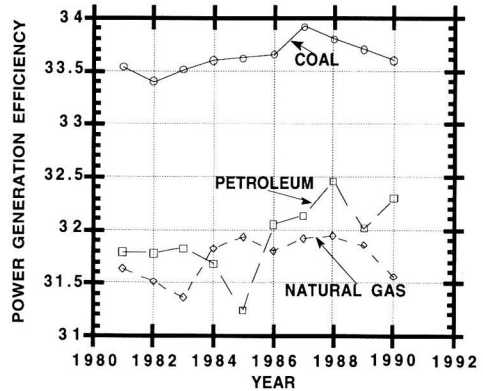


FIGURE 3. Power generation efficiency using different fuels.

On the basis of the information shown in Figures 1, 2, and 3, and on the assumptions stated above, the total amount of CO₂ produced by fossil-fueled power plants was estimated with the results shown in Figure 4. In 1990, the total amount of CO₂ produced was about 1.68 billion metric tons, an increase of 20 percent over the 1982 levels. Coal-fired facilities account for more than 90 percent of the CO₂ produced by fossil-fueled power plants. While the coal-fired power plants emit a tremendous amount of CO₂, similar amounts of CO₂ are also emitted by transportation vehicles and by industrial and residential heating equipment. The difference is precisely that there are few power plants and many automobiles, thus making power plants an obvious place to hope for economies of scale in CO₂ capture.

Several technologies for the capture of CO₂ from flue gas exist. These include chemical solvent methods, physical absorption methods, cryogenic methods, membranes, and adsorption methods. All of these CO₂-capture processes are expensive and energy-intensive [4, 9]. We evaluated these methods and found that the chemical-solvent method is commercially available and could be the most economically favorable.

Considerations of the Flue-Gas Stream

The recovery of CO₂ from the flue-gas stream is made more difficult by the nature and composition of that stream. Several factors must be considered, as discussed below.

CO₂ is present at low concentrations and thus low partial pressures. For example, when coal is burned with 110 percent

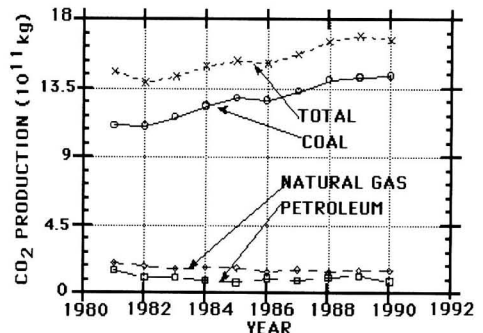


FIGURE 4. CO₂ production by U.S. Power Generation Plants.

theoretical air, CO₂ represents about 15 mol percent of the flue gas. The CO₂ percentage is lower if one considers the moisture that is already present in the coal, but the CO₂ percentage is even lower for oil (~13 percent) and natural gas (~9 percent). Most capture methods require compression of the flue gas to increase the CO₂ partial pressure for more efficient separation.

The dominant compound in the flue gas is N₂. Both N₂ and CO₂ require very low temperatures and/or high pressures to be condensed. These conditions complicate the process of separating N₂ and CO₂ from each other using cryogenic methods, both because of the potential for forming solids and because the solubility of N₂ in the condensing CO₂ will become appreciable; distillation of the N₂ from the liquid CO₂ would be required to attain high purities, if they are needed.

The large number of species present (N₂, CO₂, H₂O, H₂S, COS, CO, O₂, particulates), and the corrosive nature of some of these species, complicate all applicable separation processes. For example, even though sulfur-bearing compounds and O₂ are present in only small quantities, they undergo irreversible chemical reactions when amine scrubbers are used. These reactions result in the degradation of the solvent. When membranes are considered for the separation, difficulty in developing a single-component-selective membrane increases as the number of species present increases.

The presence of appreciable water vapor in the flue gas increases the cooling load on the separation process, and the water vapor could, under the right conditions, interact with the CO₂ to form clathrates. These solid-type (slush) structures could cause transport problems within the recovery system. Condensing water could also contain appreciable quantities of dissolved acid gases, including CO₂, which makes the water acidic and corrosive. Most of the water can be separated at much higher temperatures than are needed to separate CO₂ and N₂. Figure 5 shows the pressures to which the flue-gas stream must be compressed to permit condensing 90 percent of the water using cooling fluid at different temperatures. Figure 5 also shows the approximate cooling-fluid inlet temperature required to achieve 90 percent condensation of the H₂O and the flue-gas exit temperature required at the different pressures. For example, cooling towers supply cooling water at about 300 K (80°F) to the condenser. To achieve 90 percent drying of the flue gas stream using the 300 K (80°F) water, the flue gas has to be compressed to about 1,010 kPa (10 atm). (Incidentally, the amount of water generated when burning coal is about 4 percent of the amount of steam raised by the coal for power generation, excluding the moisture present originally in the coal). Furthermore, the necessary drying levels to prevent corrosion are achieved using desiccants, after the bulk

of the water is condensed by conventional means. Solid desiccants and liquid absorption materials, such as ethylene glycol, diethylene glycol, triethylene glycol, and glycerol, can be used [10, 11]. These materials are normally used at high pressures and are regenerated at temperatures in excess of 450 K (350°F).

Both CO₂ and N₂ are relatively inert gases, so only at excessively high temperatures will they react to form environmentally stable solid or liquid products that are easy to separate and dispose of.

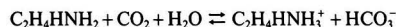
The captured CO₂ must be under pressure in order to transport it to its final sequestering destination. Today, there is an extensive network of CO₂ pipelines in west Texas and adjacent areas. Present practice maintains the pipeline pressure high. Since the CO₂ would be sequestered either underground or under water, the energy for compression cannot be wholly captured at the sequestering destination. (For example, when the pipeline pressure is 11,000 kPa (110 atm), the CO₂ can be submerged to a 1,100-m depth below the ocean surface. Note that, at 11,000 kPa, CO₂ is essentially a liquid, its critical point being 74 atm and 88°F.) The compression energy applied to the N₂ portion of the flue-gas mixture, prior to the CO₂ separation, may be recoverable in certain designs. The N₂-rich stream may be heated and expanded in a gas turbine to produce mechanical work.

The quantity of CO₂ emitted by power plants is more than 30 times greater than the quantity used in commerce. Therefore, the cost of recovering CO₂ cannot be offset by the market value of the recovered CO₂.

TECHNOLOGIES FOR CO₂ CAPTURE

Chemical Solvent Method

Chemical stripping of CO₂ involves one or more reversible chemical reactions between CO₂ and another material (such as: mono-, di-, or tri-ethanol amine; di-isopropanol amine; sodium hydroxide; sodium carbonate; or potassium carbonate) to produce liquid or solid species that, upon heating, break down to liberate CO₂ and regenerate the material reacted with CO₂. For example, the monoethanol amine (MEA) processes can be represented by the following reversible reaction:



Typical processes include ADIP, ALKAZID (M & DIK), BENFIELD, CATAcarb, ECONAMINE, MDEA, SEABORD, VACUUM CARBONATE, SNPA-DEA, SULFIBAN, SULFINOL, GIAMARCO-VETROCOKE, and STRETFORD. Many of these processes are in full-scale operation for the removal of acid gases, including CO₂, from natural gas reservoirs, ammonia production plants, and other applications. Dow Chemical Co. developed the Gas/Spec FT-1 amine-based process in the late 1970s, which was later known as the ECONAMINE process [12]. In 1978, an 800-metric tons per day amine-based plant was started up to recover CO₂ from flue gases. A 200 metric tons per day unit was started up in January 1991, and another 300-metric tons per day plant was started up in March of the same year [13]. Two other amine-based pilot plants were constructed and tested in Canada [14]. Experience with these and other plants identified three major problems: (1) solvent degradation due to irreversible reactions with O₂, SO_x, and COS; (2) corrosion in the absorber and the regenerator; and (3) operating difficulties caused by variable operating conditions. Corrosion inhibitors and additives brought these problems under acceptable control.

Most of the energy consumed by these processes is used to raise steam at pressures about 445 kPa (50 psig). The steam is used in the solvent regeneration process. The energy-intensiveness of these processes is partly related to the low absorption capacity (CO₂ absorbed per unit mass) of the solvents,

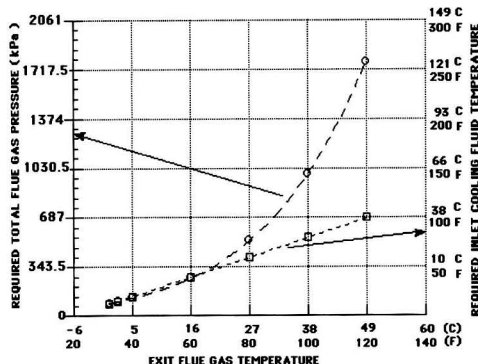


FIGURE 5. Pressure to which flue gas must be compressed to achieve 90 percent drying using different cooling-fluid-inlet temperatures.

because all of the aqueous solutions have to be heated to higher temperatures to liberate the captured CO₂. These systems require electric energy for pumping the solvent and for compressing the gas and cooling water for cooling the weak solution after the regeneration process.

Energy savings can be realized if a solvent that has high absorption capacity at moderate temperatures and atmospheric pressure can be developed. The higher the absorption capacity, the less the quantity of solvent required to handle a given gas stream, and, consequently, less energy will be required for regeneration, pumping, and cooling. Smaller and less costly equipment will be required. A solvent that can be regenerated at lower temperatures stands a better chance of being able to use waste heat instead of extracted steam from the turbine, which results in lower turbine power output.

Regeneration at elevated pressures could also be advantageous because the resulting CO₂ will be at high pressure. This requires a solvent that can be regenerated at high temperatures without thermal degradation.

Another alternative for saving energy would be to develop a thermally stable solvent that can be converted to superheated vapor, after regeneration at high pressure, and used as the working fluid in an organic Rankine bottoming cycle, instead of wasting the heat used in the regeneration process. This concept will be particularly attractive when used to recover CO₂ from the exhaust of a gas turbine, because the solvent bottoming cycle could be driven by heat available in the turbine exhaust. A simplified schematic diagram of such a concept is shown in Figure 6.

Published data [9] indicated that retrofitting a coal-fired power plant with an ECONAMINE FGSM system for 90 percent CO₂ removal and a Thiosorbic[®] magnesium-enhanced wet-lime (mag-lime) SO_x removal process resulted in a 35 percent reduction in net power production and that the cost of the retrofitting process was greater than the initial capital cost of the power plant itself. The cost included that of CO₂ transportation to and disposal in large depleted natural-gas fields or in the ocean. The results are given in Table 1. However, to facilitate comparison with other technologies, the cost of avoiding CO₂ emissions, while providing the same electrical service, is relevant. Because MEA processes need steam, whose production generates CO₂, more CO₂ must be captured than is avoided. As a result, the cost of CO₂ avoided by MEA is approximately twice the cost of CO₂ captured. On the basis of available data [9], we estimated that the net economic impact of capturing and disposing of CO₂ was an increase in the cost of electricity production from 46 to 140 mills/kWh, an important part of which is due to compression and drying.

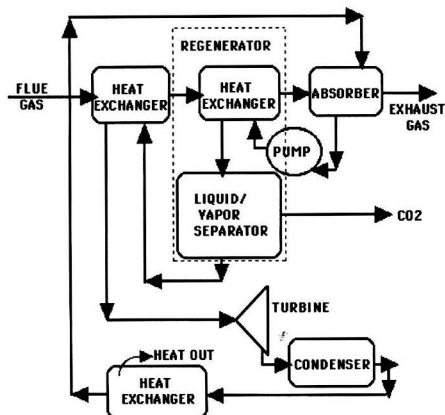


FIGURE 6. Integrated solvent regenerator/bottoming cycle.

Table 1 An ECONAMINE System Integrated with a Conventional Pulverized Coal-Fired Power Plant

Process Subsystem	Cost ^a (\$1,000 kg of CO ₂ Captured)		
	Capital	Energy	Total
ECONAMINE	10	12	22
CO ₂ Compression and Drying	4	5	9
Cycle Modifications	6	—	6
CO ₂ Pipeline	15	—	15
CO ₂ Disposal	5	—	5
Total	40	17	57

^a Discount rate is assumed to be 17.4 percent, and electricity cost is \$0.05/kWh. Source: Reference 9; data used with permission of the authors.

Physical Absorption Methods

Physical absorption is a bulk phenomenon. Inorganic and organic liquids may be used to preferentially absorb some gaseous species, separating these species from the gas mixture. The absorption process depends on the operating temperature and pressure, as well as on the nature of the gases and the absorption liquid. The absorption liquid is regenerated by increasing its temperature (temperature swing) and/or reducing its pressure (pressure swing). High-boiling solvents that have high partial pressures are preferred in order to keep solvent losses to a minimum and to prevent contamination of the released gas with solvent vapors.

Organic solvents that are commonly used include propylene carbonate (Fluor process), n-methyl-2-pyrrolidone (NMP-PURISOL), methanol (RECTISOL), dimethyl ether of polyethylene glycol (DMPEG-SELEXOL), and sulfolane (SULFINOL). Many of these processes are practiced on commercial scale. The inorganic solvent suggested for CO₂ scrubbing is sea water.

The absorption capacity of organic and inorganic solvents for CO₂ increases with increasing pressures and with decreasing temperatures. Because the partial pressure of CO₂ in the flue gas is low and the flue-gas temperature is high, the physical absorption method does not appear likely to compete with the chemical solvent method for processing the flue-gas stream. Dissolution of other flue-gas constituents, mainly H₂O, is expected to adversely impact the absorption of CO₂. Particulates in the flue gas could also cause rapid degradation of the absorption material unless the material is frequently filtered to remove the trapped particulates. These particulates could also create pumping problems.

This process could, however, be a very efficient approach for processing such high-pressure CO₂-rich streams as those encountered in advanced power generation systems, as for example, the O₂-blown coal gasification/combined cycle [4, 9]. Therefore, as we stated earlier, even though the physical-absorption process does not appear promising for capturing CO₂ from the flue gas of conventional power plants, it could be a very efficient and economical approach for CO₂ capture from emerging power-plant streams.

Cryogenic Methods

Cryogenic separation of CO₂ from combustion-gas streams involves multistage compression, followed by cooling of the compressed gas after each stage, and eventually, expansion of the cool, high-pressure stream to cause a large drop in temperature. As a result of this process, CO₂ will be liquefied, or even solidified, and separated from the gas phase. A distillation (fractionation) column may be required to separate dissolved impurities from the product CO₂. After CO₂ separation is

accomplished, the effluent stream will consist essentially of N_2 and the excess O_2 used in the combustion process. Therefore, the key question is how does this method compete, in terms of energy consumption and cost, with conventional (cryogenic) upstream air-separation systems, as both lead to essentially the same results.

The gas compression/cooling process may be supplemented with a conventional refrigeration cycle to provide additional cooling to permit the condensation of CO_2 with less gas compression at higher temperatures. The liquefied CO_2 can be pumped to the desired sequestering pressure, if necessary. This combination will also eliminate the risk of solid CO_2 formation in systems that are not designed to handle solids. The residual N_2 gas, which will be at high pressure, can be heated to high temperature and expanded in a multistage gas turbine with reheat to provide at least part of the power consumed in the compression process. This alternative is expensive in terms of capital cost, but it will minimize any reduction in output of the power plant as a result of CO_2 recovery.

The optimum total stream-pressure/refrigeration temperature may be determined analytically. Determination of the optimum pressure should take into consideration the solubility of N_2 and the acid gases (SO_x , COS, NO_x) in the liquefied CO_2 . Even though the acid gases will have a minimal impact on the mass and volume of the CO_2 product, they could reduce the usefulness of the CO_2 as a commercial product or impact the final disposal. In the presence of water, the acid gases exacerbate the corrosion problem in the transportation pipelines. The presence of SO_x , COS, and NO_x may also limit the options available for sequestering the CO_2 after it is captured. Design of cryogenic systems for the separation of CO_2 should also address the potential formation of such solid structures as CO_2/H_2O clathrates, ice crystals, and solid CO_2 particles or flakes, which could cause plugging problems. The presence of particulates is another concern when considering cryogenic separation of flue gases, especially those gases generated by coal combustion.

Cryogenic separation of CO_2 from the combustion products of utility boilers is an energy-intensive process. It is estimated that the energy penalty will be in excess of 50 percent of the coal energy. Therefore, this process appears uneconomical [4]. However, it has received little attention and deserves more before it is dismissed.

Membrane Systems

Membranes are generally solid porous, semiporous, or non-porous structures through which some of the species in a mixture permeate, leaving other species behind. In another type of membrane, called a liquid membrane or a gas-absorption membrane, the solid porous structure is impregnated with a liquid that is capable of dissolving the species whose permeation is desired, to assist in permeation of that species through the membrane [15, 16]. Microfiltration membranes are in the widest application, while gas separation membranes are used the least [17].

Two criteria of a good membrane separator are selectivity and high permeability or mass flux (the rate at which species permeate or cross from one side of a unit area of the membrane to the other). Unfortunately, the two criteria are inversely related for the common polymeric membranes. The permeability of the membrane depends on many factors, including the chemical potential gradient of the species being separated [17, 18, 19, 20]. This gradient develops as a result of gradients in one or more of the following parameters: partial pressure, concentration, electrical potential, or a combination of these. The mass flux depends also on the nature and design of the membrane itself.

Flue-gas streams generated by coal combustion are composed of many species present in different concentrations, each having its own solubility in and diffusivity through a membrane

material. For example, CO_2 , H_2S , and H_2O have reasonably high solubilities in membrane materials at moderately low partial pressures, but O_2 and N_2 have high diffusivities in the same materials. Therefore, because the overall permeability depends on both of these parameters, the development of a CO_2 -selective membrane system for such a stream is not an easy task. Multistage separation will definitely be required to achieve adequate separation. The flue gas can be cooled, dried, and compressed prior to coming in contact with the membrane system. This reduces the problem of separating CO_2 from N_2 . Several polymeric materials can be used to achieve substantial separation of CO_2 from N_2 . Sluijs [20] reported that cellulose acetate polymers can have a CO_2/N_2 selectivity (ratio of the permeability of CO_2 to the permeability of N_2) of about 66.5. This value means that substantial separation of these two gases is technically feasible, although a selectivity of over 200 is needed for adequate separation. Concentration of the CO_2 in the flue-gas stream by such membranes is probably a more realistic goal. The presence of fine (approximately micron size) particulates under acidic conditions could result in performance degradation and increased maintenance requirements.

Membranes can be energy-efficient when excessive compression is not required to attain a practical pressure gradient of the targeted species across the membrane. The relatively low CO_2 pressure in the flue gas dictates the need for compression to increase the partial pressure of the gas constituents and to compensate for the pressure loss across the membrane. Another concern with membranes is the ability to maintain a sufficiently low partial pressure of CO_2 on the downstream side of the membrane. With the exception of water vapor as a potential sweeping gas for the separated CO_2 (which could be easily separated by condensation), evacuation of the downstream chamber or absorption of the CO_2 into a chemical or physical absorption material appear to be the only obvious alternatives. These alternatives are energy-intensive. However, the evacuation alternative could be integrated with the product compression step, provided that the product is low in non- CO_2 constituents.

PHYSICAL ADSORPTION SYSTEMS

Physical adsorption of gases on solid adsorbents (such as activated carbon) is a surface phenomenon in which a few layers of the adsorbed gas are held by weak surface forces. The capacity of an adsorbent for a given gas depends on the operating temperature and pressure. The higher the partial pressure and/or the lower the temperature, the greater the adsorption capacity of the system. The key issue for commercial application of these systems is the surface area required per unit mass or volume of adsorbed gas. However, these systems are simple, and their operation and regeneration (temperature swing or pressure swing) can be energy-efficient.

Because the adsorption process is highly sensitive to temperature and pressure, cooling and compression of the flue-gas stream is necessary. Competition between CO_2 and other flue-gas constituents, especially H_2O , for the active adsorption sites is expected to reduce the adsorption of CO_2 , because water vapor will be adsorbed preferentially. In addition, the capacity of such systems for CO_2 adsorption is small. Particulates in the flue gas could also cause gradual deactivation of adsorption sites because of the difficulty expected in removing particulates by heating or depressurization. Therefore, we do not expect this system to compete very well with absorption systems for the separation of CO_2 from the flue gas of conventional coal-fired power plants.

CONCLUSIONS

We believe that the chemical absorption system is the most

promising technology for separation of CO₂ from the flue gas of a conventional coal-fired power plant. Cryogenic methods appear to be a distant second, but deserve more attention. Although physical absorption systems appear very promising for Integrated Coal Gasification-Combined Cycle and fuel-cell plants because of the higher pressures of CO₂ encountered in plants operating with these technologies, physical absorption systems lag behind chemical absorption methods when considered for application in conventional power plants.

The chemical absorption (amine) process is still expensive and energy-intensive, and substantial improvements in performance and cost are necessary to minimize the increase in the price of electricity that would result from the use of this technology.

RECOMMENDATIONS

The development of an improved chemical solvent is essential to improving the performance and reducing the cost of CO₂ capture. Such a solvent should be environmentally safe and should have:

- High absorption capacity at moderate temperatures and pressures. An absorption capacity of about 1 kilogram of CO₂ per kilogram of solvent is a reasonable target.
- High vapor pressure and thermal stability at elevated temperatures. The pregnant solution can then be pumped to high pressure, followed by heating to high temperature, to liberate the CO₂ at high pressure and thus avoiding recompression of the CO₂, all without losing appreciable amounts of solvent. A high-vapor-pressure solvent that can also be used as the working fluid in an organic Rankine bottoming cycle will have the added benefit of allowing the regeneration energy that was applied to the solvent to be used for power production instead of wasting it.

ACKNOWLEDGMENT

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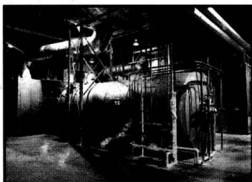
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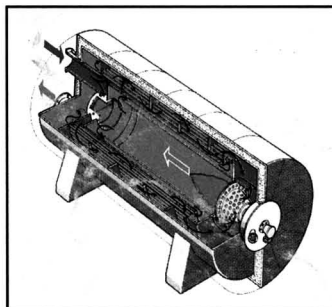
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