

ENVIRONMENTAL PROGRESS

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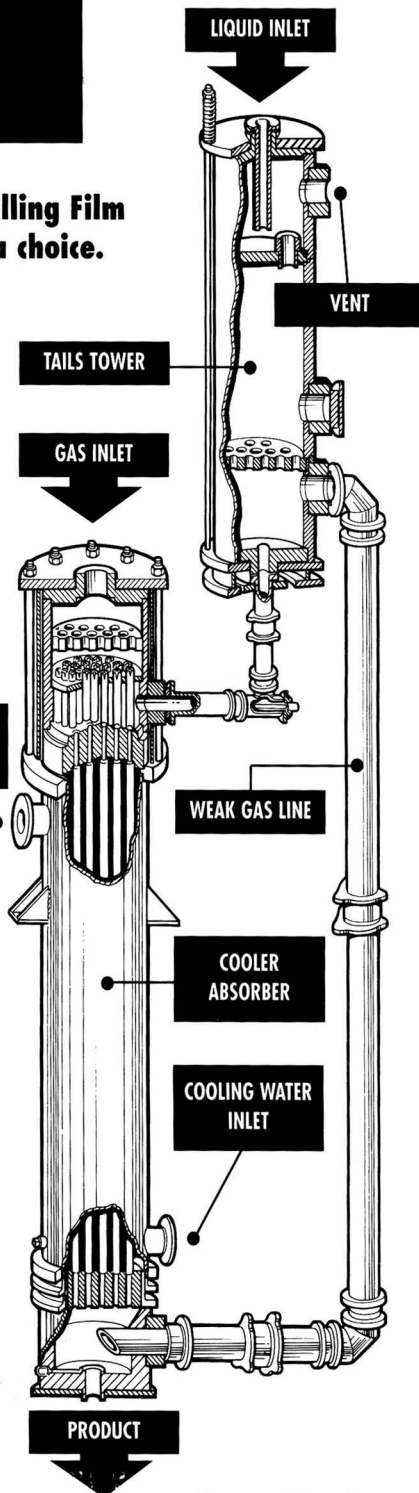
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Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multifaceted aspects of the pollution problem. It will provide thorough coverage of abatement, control, and containment of effluents and emissions 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: Crystal clear clarifier at the Eagle Mine wastewater treatment plant near Mintum, Colorado (see story on page M7).
Photo courtesy of McLaughlin Water Engineers Ltd., Denver, Colorado.

Cover Design: Joseph A. Rosetti

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Cleanup of Contaminated Groundwater: A Major Policy Dilemma

Michael C. Kavanaugh, PhD., P.E., D.E.E.

ENVIRON Corporation, 5820 Shellmound Street, Emeryville, CA 94608

Recently, I had the privilege of chairing a National Research Council committee that addressed the policy dilemma confronting regulatory agencies overseeing groundwater cleanup at hazardous waste sites. The Committee's findings, presented in a recent report [1], delineate the collision course between society's desire to restore groundwater quality to beneficial uses and the inherent technical limitations of removing contaminants from the subsurface environment.

EPA estimates that over 3,000,000 sites may require remediation in the U.S. Present worth cost estimates of remediation range from \$250 billion to \$1 trillion 1993 dollars, depending, in part, on cleanup levels (based on state non-degradation policies), drinking water standards (the predominant cleanup goal) or, in a few cases, risk-based levels throughout the designated plume boundaries.

The predominant technical strategy to meet cleanup goals is application of "pump and treat" technology or forced gradient water pumping to remove contaminants from the groundwater and aquifer solids. The number of pump and treat systems in the United States is unknown, but many exceed 3,000. As summarized in the NRC report, studies conducted by EPA, the American Petroleum Institute, Oak Ridge National Laboratory, and many researchers have unequivocally shown that the ability of this technology to achieve low cleanup levels is limited.

Although the Committee reviewed data from only a small number of sites (77, in fact), the range of conditions encountered reflects the technical challenges at most sites. Based on data provided through 1992, health-based cleanup levels had reportedly been achieved at only eight of the sites. Given longer time frames, more sites may be restored using pump and treat, but, in most cases, steady-state (asymptotic) levels had been achieved that exceeded the target levels.

The Committee concluded that technical constraints inhibiting complete restoration include strongly adsorbed compounds, compounds in low permeable zones, slow mass transfer, dense non-aqueous-phase liquids (DNAPLs), and the difficulties of characterizing and remediating highly heterogeneous geologic environments. Pump and treat is not effective for remediation when these factors are dominant, but pump and treat can effectively contain contaminated groundwater, and can often significantly reduce the size of contaminant plumes.

The Committee categorized sites based on two key characteristics influencing restoration, the hydrogeologic properties of the aquifer, and the chemical properties of the contaminants. Cleanup appears feasible at sites with homogeneous aquifers, containing mobile, and aerobically degradable or volatile compounds where releases are recent. Unfortunately, probably only a small fraction (less than 20%) of the sites fall into this category. On the other

hand, many sites pose such difficult challenges (such as DNAPLs in fractured bedrock) that neither existing nor developing technologies appear capable of achieving complete restoration. The majority of sites fall in a category where complete restoration is improbable but not impossible using current technologies. In testimony before a Congressional committee during SuperFund reauthorization, I stated that more than 80% of the larger sites probably fall in these latter two categories.

The Committee recommended that regulatory agencies use such a categorization approach for setting cleanup standards and selecting technical strategies for cleanup at the earliest possible stage in the remediation process. EPA's current policies, while generally recognizing technical limitations to complete restoration, do not reflect the large number of sites where technical infeasibility may require alternative cleanup strategies.

A successful technical strategy at many sites will include physical or hydraulic containment, active remediation where technically practicable, and maximum exploitation of intrinsic transformation processes in the subsurface. Contaminants will remain on site for many

years, and, in many cases, indefinitely. Regulatory agencies have not adequately addressed the issue of long-term monitoring and maintenance at such sites. This is a particularly sensitive issue for affected community groups who do not have confidence that institutional mechanisms are sufficiently robust to provide long-term protection.

What is the significance of the NRC report in the current debates over groundwater restoration? It is my hope that the findings of the report, which represent a consensus of many different stake-holders, and which were subject to extensive peer review, will result in dramatic decreases in cost for groundwater cleanup. For the regulatory community, the report should narrow the gap between reality and wishful thinking. Regulators should move forward with the difficult process of incorporating technical infeasibility into the process of setting cleanup levels for groundwater, and into the remedy-selection process. Strategies are available that will still protect human health and the environment, but at significantly lower costs.

For owners and operators, it is clear that new technologies are needed to accelerate the removal of contaminant mass from aquifers and other source areas. A combination of enlightened regulatory strategies, such as the development of a non-attainment zone policy in California, and improved mass-removal technologies may break the log jam inhibiting development of brown-field properties, or the sale of other properties impacted by contaminated groundwater.

Chemical engineers well know that soil makes for a very poor reactor design. The challenge to the technical community is to develop optimum technical combinations that can assure effective mass removal, effective containment if mass cannot be removed, and that can exploit naturally occurring processes in the subsurface. Protecting human health and the environment from groundwater contamination in a cost-effective manner should be within our grasp if all reasonable stakeholders can accept the findings of the NRC report. If achieved, this will be the most significant legacy of the voluntary efforts made by the nineteen experts on the NRC committee.

Michael C. Kavanaugh, Ph.D., P.E., D.E.E., is a Principal at ENVIRON Corporation. He has 24 years of experience in all aspects of environmental engineering with particular expertise in hazardous waste management, soil and groundwater remediation, process engineering, industrial waste treatment, technology evaluations, compliance and due diligence auditing, water quality and wastewater treatment, and water reuse. He has authored or co-authored over 50 technical papers and has chaired the National Research Council committee addressing alternative strategies for remediation of contaminated groundwater. He is a registered chemical engineer in several states, and a Diplomat of the American Academy of Environmental Engineers (AAEE). Dr. Kavanaugh is also a Consulting Professor of Environmental Engineering at Stanford University. He received his PhD in Civil/Sanitary Engineering from the University of California at Berkeley. He has B.S. and M.S. degrees in Chemical Engineering from Stanford and UC, Berkeley, respectively.

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SRI International Wins Monsanto's \$1 Million Challenge

Last August, Monsanto Company challenged the world scientific community to develop a new water-pollution-control technology for solving a specific problem of recovering ammonia from wastewater streams that also contain certain organic chemicals.

A proposal submitted by SRI International of Menlo Park, California, was just selected as the most promising potential solution to Monsanto's \$1 million challenge. SRI's scheme was chosen from 182 qualified proposals, which were reviewed and ranked by a panel of six scientific and engineering experts organized by the American Institute of Chemical Engineers' Center for Waste Reduction Technologies (CWRT).

SRI's Dr. Abhoyjit S. Bhowan, Dr. Luke V. Schneider, and Ronald M. Smith combined their technical expertise in chemical engineering, bioprocessing technology, petrochemicals and energy to develop the winning solution.

Earl Beaver, director, Waste Elimination, for Monsanto, and chair emeritus of CWRT said "In addition to the proposal developed by SRI, we also received numerous other high-quality proposals from other firms, government agencies, universities, and individuals. These came from 15 countries, from Australia to Zimbabwe, and every continent except Antarctica.

As the winning proposal, SRI International will receive a research contract and \$500,000 in funding to develop and demonstrate the effectiveness of its proposal in a laboratory. It will receive a second \$500,000 if the results can be applied successfully to Monsanto manufacturing sites

Jack Weaver, director of CWRT, said that, although many outstanding proposals were submitted, the SRI proposal stood out in terms of technical innovation and economic feasibility. He also said that the Center is considering, and hopes to support, additional research in ammonia recovery based on some of the remaining proposals.

Innovative Heavy-Metals-Removal Process Developed for Superfund Site

In the mid-1980's, Eagle Mine, a former zinc mine near Mintum, Colorado, was identified as a Superfund site because of contamination of the adjacent Eagle River. The pollution originated from accumulated mining wastes.

In 1988, the former owner began a complex site cleanup that consisted primarily of relocating, consolidating, and capping several million tons of tailings material. In late 1989, metals-contaminated mine water began seeping from the old mine workings and reached the Eagle River. A 200 gal/min interim water treatment plant was installed to treat the collected seepage but it had operational problems and required considerable maintenance to operate efficiently.

In August 1989, McLaughlin Water Engineers Ltd., of Denver, Colorado, was retained to identify treatment-process improvements or alternative treatment solutions. MWE recommended that a new plant, one sensitive to the specific treatment needs of the influent, be designed.

A laboratory study was undertaken to develop a process suitable for treating heavy metals-contaminated water. The plant had to be designed, constructed, and operational as quickly as possible. Design criteria for the new plant consisted of existing discharge permit limitations, which specified maximum contaminant levels in the discharge, and a maximum average monthly flow rate of 200 gal/min.

The water treatment plant was completed in January 1991 (six months after bench testing). In 1994 a sludge dewatering facility was added. The dewatering facility consists of two 48-inch plate and frame presses and associated pumps, piping and compressors. The presses rest on a large steel frame above two dump truck bays. The dewatering facility converts the 7 percent slurry into a cake having a solids content of 45 percent.

The clearness of the clarifier effluent (pictured on the cover of this issue) is a result of MWE's

patented heavy-metal removal process. It produces an effluent water quality exceeding EPA BAT levels using a single clarification step, without the need for filtration and without significant post-precipitation and scaling. Although developed for water with high sulfates and metals concentrations, the process has proven exceptional performance on a wide range of water qualities and a variety of heavy metals.

The process uses two primary chemicals: lime $[Ca(OH)_2]$ and soda ash $[Na_2CO_3]$, in two separate reactions. While traditional treatment chemicals are used, the process is innovative because the two-stage reaction sequence produces different solids and does not use intermediate clarification.

The work of McLaughlin Water Engineers Ltd., at the Eagle Mine was recognized by the Colorado Mined Land Reclamation Board (MLRB) in 1993 for outstanding reclamation at a Colorado mine.

Hazardous Materials Handling Standards Issued

The first national quality standards defining the knowledge and skills necessary to effectively handle and manage hazardous materials have been released by the National Skills Standard Project for Hazardous Materials Management Technology.

"The HMMT standards reflect a growing national concern about the level of skill and the competence of hazardous-materials workers, and the educational preparation necessary to equip them to function in an increasingly technologically advanced industry" said Jim Johnson director of the Hazardous Materials Management Technology Project.

The project is funded by the U.S. Department of Education and managed by the Center for Occupational

Research and Development. "This is a significant step for environmental and industrial safety in the United States" said Dan Hull CORD's president.

Until recently, the United States has been the only major industrialized nation without national standards to define the skills required for industrial occupation, including hazardous materials management technology, he adds.

A coalition of experts in environmental technology donated hundreds of hours to the project and shaped technical aspects of the standard, Johnson said. In addition, more than 100 corporations were involved.

Among the professional societies who took part were the Hazardous Materials Control Resources Institute, the National Association of

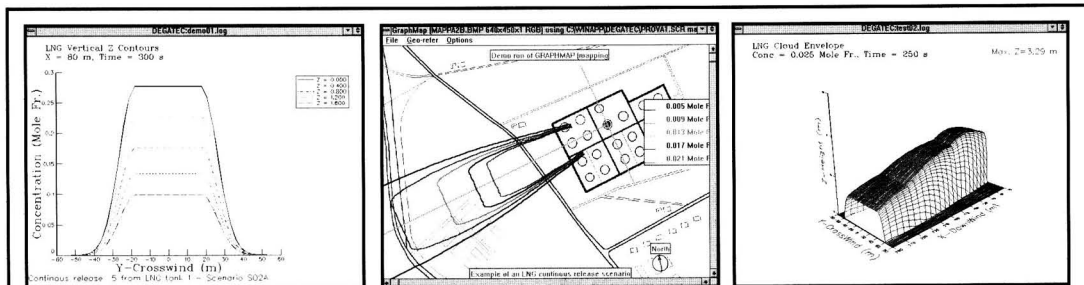
Environmental Professionals, the National Environmental Health Association, the National Environmental Training Association, and the Partnership for Environmental Technology Education.

For more information contact the Center for Occupational Research and Development (CORD), P.O. Box 21689, Waco, Texas 76710.

corrected 16 Jan. 96/A

Erratum

In "Design Concepts for Biological Treatment of Industrial Wastewater" *Environmental Progress*, 14, (1), pp. 1-8 (1995), Guy N. Matelli's name is spelled incorrectly. The authors should read: Ronald W. Capps, Guy N. Matelli and Michael L. Bradford.



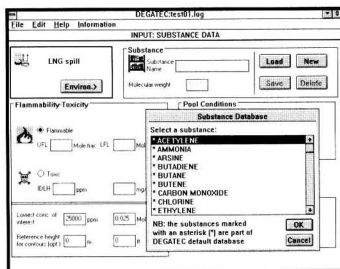
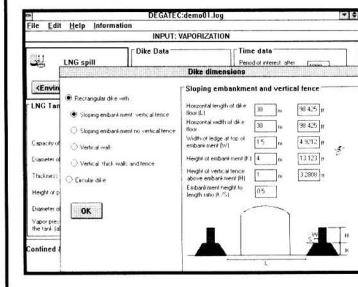
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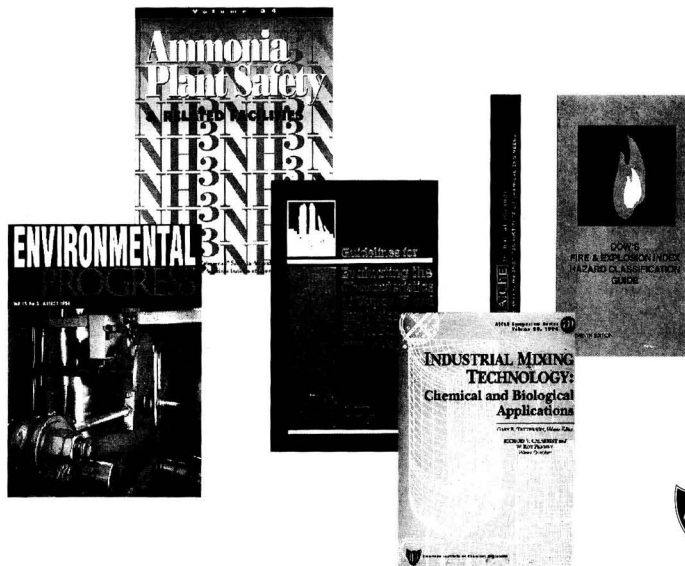
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Washington Environmental Newsletter

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

The Clean Air Act Amendments of 1995: Heading Toward Reality...

Will the Congress open the Clean Air Act again? That's a question being asked by industry representatives, environmental advocates, state officials, and even some members of Congress. With each passing day, there seems to be more support for doing so. As EPA continues to implement the law through its regulations there are mounting concerns developing in both the public and private sectors over the consequences of those regulations.

Congress last visited the Clean Air Act almost five years ago when it adopted, after several years of debate, the Clean Air Act Amendments of 1990. The revised statute was signed into law by then president George Bush on November 15, 1990.

The 1990 Act

The new Clean Air Act incorporated some of the most-far-reaching changes in air policy ever enacted. The various titles of the bill address ozone, carbon monoxide, and PM10 nonattainment, acid rain, toxic air pollutants, and CFC's. New standards and procedures to control emissions of these pollutants were adopted. For example, lower limits were placed on motor vehicle emissions. Gasoline compositions were changed, toxic-pollutant emissions standards were established at very low levels, major reductions in sulfur oxide (SO_x) and nitrogen oxide (NO_x) emission levels were set, and complicated permitting procedures were specified for all processing facilities.

The Public

The amended Act also includes provisions that impact the driving public directly. Now that the provisions are being implemented, they have caused some members of Congress to call for a reexamination of the Act. In many areas of the country, state and local authorities have raised objections to EPA's centralized Inspection and Maintenance (I&M) and employee trip reduction programs, because of complaints from their constituents. The statute requires that states implement enhanced I&M programs in all serious, severe, and extreme ozone nonattainment areas, and all moderate and serious carbon-monoxide nonattainment areas. In severe and extreme ozone nonattainment areas, employers of 100 or more persons are required to adopt a program to reduce the number of work-related vehicle trips traveled by their employees by developing programs to increase average passenger occupancy per vehicle by no less than 25 percent from the current average vehicle occupancy. In several areas these programs have either been put on hold or modified.

Complaints have also come from motorists who are finding that they are paying higher prices for the more costly reformulated and oxygenated gasolines required in the worst ozone nonattainment areas of the country, and all of the carbon monoxide nonattainment areas. Parts of the country that had opted into the program voluntarily, quickly opted out once the higher-priced reformulated gasoline hit the street. Even Milwaukee, where reformulated gasoline is mandatory, is petitioning EPA so that it can discontinue using the cleaner-burning fuel. Industry sources say that these complaints seem to be coming from the same public that several years ago, when polled, said they were willing to pay a higher price for cleaner air.

The EPA

EPA claims these programs will result in significant air-quality improvements, but consumers are unhappy with having to pay higher prices at the pump, wait in inspection lines, and carpool. Coincidentally, these provisions went into effect on January 1, just as the new Republican majority was arriving in Washington, DC. The increased burden on the public are contrary to the Republican's agenda of reducing the federal government's intrusion into peoples' lives.

The Congress

Representative Joe Barton (R-TX), the new Republican Chairman of the House Oversight and Investigations Subcommittee of the House Commerce Committee, has announced that he will hold oversight hearings on all titles of the Clean Air Act Amendments of 1990. As of this writing he has already conducted hearings on I&M and employee trip-reduction programs. Representative Michael Bilirakis (R-FL), Chairman of the Health and Environment Subcommittee, which has jurisdiction over the Clean Air Act, has indicated that he will also be holding hearings. Issues that many would like to see addressed are: the Title V Permits provisions, proposed regulations on enhanced monitoring; new vehicle requirements in the ozone transport region. The health effects of oxygenates required are reformulated gasolines; refinery MACT for small and midsize refineries and the ozone standard and the manner in which areas are designated attainment or non-attainment, to name a few.

Although the Act has not been amended as such, Congress has passed legislation in both Houses that could affect the implementation of the I&M and employee trip-reduction programs. Using a backdoor approach, i.e., a legislative maneuver to deny funds to implement programs, the House and Senate Appropriations Committees have approved amendments to a fiscal year 1995 recession funding bill that could prohibit EPA from spending federal dollars to implement these two programs. The House bill also includes language that would prohibit EPA from spending money to complete work to implement the mandated California Federal Implementation Plan (FIP) for correcting the ozone problem in the Los Angeles area. Before the recession legislation becomes law, the differences in the two bills must be resolved by a House/Senate conference, be approved again by both bodies, and signed into law by the President. The latter is still uncertain, and the conference could take some time to complete.

The Industry

Whereas there is clearly support for reopening the Act from some industries there is concern expressed from others about the Act being opened at this time. A spokesman from the electric utility industry indicated that they would be opposed to any changes to the Title IV provisions, as they are well along in meeting their SO_x and NO_x emission reductions required by the Act. A primary concern within the utility industry would be a legislative requirement to further reduce NO_x emissions in areas of high ozone concentrations. (Under certain conditions NO_x is an ozone precursor; in others it scavenges ozone.) In the oil industry, Chevron U.S.A. Products Co. president Dave O'Reilly has recently called for "changing the oxygenate rule in federal reformulated gasoline," which would require that the Act be opened to amendment. Others in this industry, though, are reluctant to see the fuels requirements addressed.

The Consensus

One way or another it appears to us that the Congress is going to do something about provisions in the Clean Air Act that will bring about change.

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A Review of AIRSCAPE Program for the ISC2 Model

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Introduction

Air quality models have been systematically used as official decision-making tools for the preparation of State Implementation Plan (SIP) revisions. The industry may be required to report the estimated impact of its emissions under the preview of the Prevention of Significant Deterioration (PSD) or the New Source Review Program or Title V permit program of the 1990 Clean Air Act Amendments. The impact of the non-reactive pollutants is estimated using Gaussian models. These models, which are the most widely used are categorized by two levels of sophistication—screening models and refined models. Screening models provide conservative estimates of air quality impact, while more accurate estimate of the source impact and the effectiveness of different control strategies is provided by refined models.

ISC2 is one of the widely used Gaussian refined model, which is among the “preferred” models categorized by Environmental Protection Agency (EPA). It is used to assess pollutant concentrations from a variety of sources associated with an industrial source complex. Its use has been deemed appropriate by the regulatory agencies for industrial source complexes, rural or urban areas, flat or rolling terrain, transport distances less than 50 km and one hour to annual averaging times. The model can account for the following: settling and dry deposition of particulate; down wash; area, line and volume sources; plume rise as a function of downwind distance; separation of point sources and limited terrain adjustment. It operates in both long term and short term modes (ISCST2 and ISCLT2).

The running of ISC2 programs would require preparation of the input file as per the format prescribed by ISC2 manual [1]. In this format, the specification of the options and input data is done by making use of the keyword/parameter approach. The keywords specify the type of option or input data being entered on each line of the input file. The parameters following the keyword define the specific options selected or the actual input data. Certain keywords are mandatory and must be present in every run stream file, whereas other keywords are optional and are only needed to exercise particular options. This calls for thorough knowledge of the input format intricacies.

Overall the file preparation procedure is both time consuming and tedious for the modelers. In addition, the error detection and correction of the input file is difficult.

The problems associated with the preparation of the input file

has prompted several software developers to provide graphic interfaces to the ISC2 model. These interfaces, in addition to aiding preparation of input files, run the ISC2 using the USEPA's ISC2 executable file. The graphic interfaces make the whole process easy to modelers and helps in conceptualizing the problem to novice modelers. This paper reviews one such software, namely AIRSCAPE, developed by Alpha Terra Inc. The software can be obtained from Alpha Terra Software, 725X Wood lake Road, Kohler, Wisconsin 53044 (Telephone: 414/457-9190) for an introductory price of \$779 (both ISCST2 and ISCLT2 professional versions) for commercial establishments, and \$393 for government agencies.

Description of Airscape Interface

AIRSCAPE is a windows based program for the development of the ISC2 input files. It creates ISC2 input files with graphical user interface in windows. Sources, receptors, boundaries and buildings are created through point and click methods on display screen. These are developed on screen as colored icons within a user defined Cartesian coordinate system.

The hardware requirements for AIRSCAPE [2] are:

- 80386, 80486, or Pentium™ based IBM® or compatible
- 4Mb RAM minimum
- 1.44 meg, 3.5" floppy drive
- Microsoft Windows™ 3.1

The program has provided an interactive main menu which contains the following sub menus:

File Menu: This menu is used to open, save, import, export and print files. The import option can be used to import either Building Profile Input Program (BPIP) results or AutoCAD DXF file that can be used as a base map for current project. The export option is used to export current boundary receptor information for use in SURFER®, AutoCAD®, Autosketch® and other graphic programs.

Edit Menu: This has an option to create a bitmapped image of current screen display that can be used for pasting into other applications. In addition, the menu provides options to modify source, receptor, boundary and building information.

View Menu: This is used to view the area selected for study and the type of receptor grid used it also has option to view ISC2 input, output and error files.

Run Menu: There are two ways to run ISC2 model through AIRSCAPE. The express run option runs the current project in AIRSCAPE, while the schedule run option allows for single or multiple modeling runs at any preset time.

Options Menu: The menu contains preferences option which is used to specify the path to ISC2 program (the program can be downloaded from Bulletin Board System (BBS) operated by the USEPA [3]) and BPIP program (if the program is different from one supplied in AIRSCAPE). This menu also contains the options to select the type of mouse pointer, display of rulers and DXF files. Additionally it contains utility options that allows to convert grid to discrete receptors and shift or rotate coordinates.

Pathway Menu: The pathway menu is helpful in preparing input files. It contains COntrol pathway option, SOurce pathway option, MEteorological option and OUtput option. Each of the options are used to input data into the respective pathway of ISC2 input file.

BPIP Menu: This menu helps to run BPIP and to import the results of BPIP run.

Help Menu: Help menu is used to provide on-line help regarding AIRSCAPE program. It also contains ISC2 and BPIP manuals that can be referred.

The tool bar menu allows a user to perform file management, data input, drawing and display functions, without opening pull down menus. It provides a quick way to create input file and run ISC2 model.

File controls like creating a new file, retrieving, saving and printing are each represented by icons. Clicking an icon would open the window that would require the appropriate file name to be input.

The options under the pathway main menu are also provided by means of icons and their corresponding windows. The COntrol pathway icon can be used to specify parameters such as averaging times, pollutant information, and terrain characteristics. The source pathway icon provide means to input data regarding source groups, emission units to be used in calculations and emission factors that vary with time. Various formats for emission factor option are made available. Additional formats can be added that give the user greater flexibility to manipulate the inputs. The name and kind of the meteorological file to be used can be specified through meteorological icon. The user can specify the day range for which ISC2 must be run. The last of the pathway icons, namely output options, need the user to specify the various output files that are desired.

The display screen is used to graphically represent sources and receptor grid. The area to be displayed can be adjusted using the range tool from edit menu. The sources are located on display screen with the help of coordinate display window, that specifies the coordinates of mouse location. The coordinates can be displayed either in Cartesian coordinates or in UTM coordinates. Version 2.02 includes a field of UTM zone in the range tool that

allows display of latitude and longitude coordinates, when range is set to a UTM system. The source parameters can be input into the program, as soon as a source is located, through a source window that appears, on the display screen. The type of receptor grid to be used can be selected from grid tools option in the menu. The two receptor grid types are cartesian grid (uniform and non-uniform) and polar grid (uniform and non-uniform). The terrain elevation at each receptor of the grid can be input manually or digital elevation model file can be imported into the program. Discrete receptors can also be located on the display screen. coordinates and the receptor height can be specified in a receptor window that appears on the display screen as the receptor is located. The contents on the display screen can be viewed by zoom in and out, or by 3-D display.

The buildings around the sources can be drawn on the display using building drawing tool from the tool bar menu. These buildings and their respective dimensions can be stored as a separate file that can be used as input for BPIP [4]. BPIP program gives direction specific building coordinates that are used as input to ISC2 model. BPIP module is provided in the professional version of AIRSCAPE. This program can be run from AIRSCAPE and results can be directly imported into the ISC2 input file.

ISC2 input file is divided into five functional pathways. The pathways are identified by a two character ID. They are CO, specifying overall job control options; SO, for specifying source information; RE, for specifying receptor information; ME, specifying meteorological information; and OU, for specifying output options. AIRSCAPE facilitates the input of the data in these functional pathways by representing them as icons. Input to receptor pathway is done on the display screen as already described. By selecting any of the other pathway icons the appropriate windows are displayed in which input can be specified by writing in the fields or selecting from the existing choices. The sources can be combined into groups to find the impact of sources under various combinations. AIRSCAPE lists all sources so that they can be selected with mouse to form groups in order to vary the emission rates with time, various formats given in the source option for the user to select. ISC2 model requires meteorological file as input. The procedure describing preparation of meteorological file for ISC2 model is presented by Kumar and Ranganathan [5]. The path to the meteorological file must be specified along with the station numbers and the year of the meteorological data. The period for which the ISC2 model must be run is specified in the meteorology options of AIRSCAPE program. The inputs in the output option include specification of various files and tables required by the user.

AIRSCAPE also has the capability to import the bitmap image of aerial photographs or AutoCAD[®] DXF files of plot plans or faculty maps. This feature allows the user to mark/check the location of sources and discrete receptors. The maps can also be used to trace the plant buildings with building drawing tool and record the building coordinates for running BPIP. In addition, version 2.02 has the capability to zoom in and out of the bitmap import

Table 1 The Maximum 10 1-Hr Average Ground Level Concentrations of Gaseous Pollutant Obtained from ISCST2 Run

Rank	Concentration ($\mu\text{g}/\text{m}^3$)	Date	Time (Hr.)
1	20908.33	07-27-91	0400
2	20471.94	06-18-91	0400
3	10858.62	10-31-91	0300
4	10721.00	07-15-91	0800
5	6605.15	12-28-91	0800
6	6595.78	05-21-91	0300
7	6579.88	09-01-91	0800
8	6522.07	11-20-91	1800
9	6512.56	08-05-91	0400
10	6261.53	08-11-91	0300

Note: All the maximum ten concentrations occur at (-450,100) from the main stack.

Table 2 The Highest Quarterly Average Lead Concentrations for Each Quarter.

Quarter	Obtained from ISCLT2 Run		
	Concentration ($\mu\text{g}/\text{m}^3$)	Receptor (m)	Coordinates (m)
1	1.50	125	25
2	1.26	125	25
3	1.57	100	-50
4	1.22	125	-75

to the display screen. But when importing 256 color bitmaps most computers will need to have the graphics card set to 16 bit or 24 bit.

Application of AIRSCAPE

The software package is obtained from Alpha Terra Science Inc., for the purpose of reviewing. It is loaded on an IBM personal computer clone. There were no problems encountered in loading the software through Microsoft Windows 3.1. Two test cases are developed to test AIRSCAPE ISCST2 and ISCLT2 models.

The run for ISCST2 is done using a fictitious manufacturing plant located in Toledo, Ohio. The plant is considered to emit gaseous pollutants through eight sources located in the plant's premises. All the sources are considered to be point sources. The emission rate from each source is taken as 1 g/s. The stack temperatures range from 293 OK to 850 OK. The exit velocities of these sources range from 0.1 to 9.1 m/s. The average diameter for the source stacks is 1.55m. The sources are marked on the display screen. The building drawing tool was used to draw the layout of the building. The BPIP program was run for the building input file and the results of the program were imported to the ISC2 input file. A uniform Cartesian grid (21 x 21) centered at the main source is selected using the grid tool. The spacing of the grid was taken as 100m.

The surface data and upper air data for Flint (#14826) and Toledo (#94830) respectively were downloaded from the EPA BBS, for the year 1991. An unformatted meteorological file was prepared using these two data files. The data period was set as 365 days. The ISC2 was run in the regulatory default mode and the rural option for 1 hour averaging concentrations. The results are shown in Table 1.

AIRSCAPE ISCLT2 program is also tested by considering a fictitious lead plant with 14 sources. The exit velocities range from 5.3 to 29.3 m/s, whereas the exit temperatures are within 293.15

OK to 589.15 OK. Typically the lead emissions at the plant range from 0.112 g/s to 0.00000029 g/s. Out of the 14 sources, 4 are considered as volume sources, 2 as area sources and the rest as point sources. With main stack taken as the origin, the location of the other sources are obtained. Cartesian grid (21 x 21 receptors) with a spacing of 25 m is selected. For this modeling scenario the meteorological data, consisting of one year (1985) of observations taken at Columbus, Ohio surface air station #14821 and the Dayton, Ohio upper air station #13840, are obtained from the EPA BBS. The ISCLT2 is run in regulatory default mode and urban option, to obtain quarterly average concentrations. Some of the results are given in Table 2.

Conclusion

An interface to the Industrial Source Complex Model, AIRSCAPE, was studied. During our investigation we found it to be a very useful tool to run the ISC2 model. AIRSCAPE can be used to train new employees on air quality modeling process. It is hoped that users will find it a useful tool for solving problems at their plants.

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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.

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Optimizing Remedial Action Implementation at the C & R Battery Company Superfund Site

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Adding value to hazardous waste site remediation projects during early stages is paramount to avoid unnecessarily costly design and construction issues. Privatization of the C & R Battery Company Superfund site remediation provided opportunities for large cost savings which appeared to have been excluded while the project was federally led. In governmentally-led projects, formal value engineering studies may not reduce final project costs because implementable cost saving alternatives may be rejected or ignored due to administrative objectives and pressures. Over reliance on the effectiveness of the value engineering study to find and add economics in a project may also have contributed to a less innovative design from the outset. In the case of the C & R Battery Company Superfund site, a formal value engineering study was performed at the 90 percent completion point in the Remedial Design (RD) under the auspices of the United States Environmental Protection Agency (EPA). As a result of the late point in the project at which the formal value engineering study was performed, many cost saving opportunities were lost. After privatization, re-evaluation of basic design concepts provided for tremendous cost savings, but they were limited to items which could be implemented without necessitating administrative approvals or upsetting the schedule mandated by the EPA.

A value-added approach to project execution was implemented following privatization of the C & R Battery Company Superfund site remedial action which proved more effective in optimizing the cleanup than the formal value engineering study performed while the project was led by government agencies. The value-added approach required a focus on results and a continuing re-evaluation of project features and benefits through design and construction. The value-added

enhancements minimized excavation, modified soil quality verification strategies, and reduced materials handling and other construction effort. The resulting efficiencies were made available after privatization and adding value to the project through re-evaluation of strategies. As is evidenced herein, the achieved cost savings were substantial and could have been greater had the value-added approach been pursued earlier in the project.

BACKGROUND

The C & R Battery Company Superfund site, located south of Richmond, Virginia, was a former lead reclamation facility for automobile and industrial batteries. The reclamation process involved breaking or sawing the battery casings, draining the acidic battery liquids into an unlined surface depression near the center of the site, separating the battery casings from the lead cores, and stockpiling the lead cores for re-melting by an off-site processor. The battery breaking and sawing activities reportedly occurred at several locations on the five-acre site, contaminating soil to various shallow depths and with a wide range of lead concentrations. The contaminated soil was spread to adjacent woodlands and neighboring commercial properties by airborne transport and possibly from former site grading activities encompassing six additional acres.

The project team privatized the EPA-led cleanup after the Remedial Design (RD) was virtually complete. The EPA, through its contractors, performed extensive field investigations, assessments of the human health and environmental risks, and feasibility studies of potential alternatives for cleaning up the site. Following these phases, the EPA issued a Record of Decision (ROD) [1] requiring excavation, on-site treatment through stabilization and off-site disposal of approximately 38,000 cubic yards (29,000 cubic meters) of lead-contaminated soil. The EPA-estimated cost for the remedy was \$16 million including construction costs, EPA oversight costs and engineering.

The site soil consisted of a 2- to 4-foot (0.6 to 1.2 meters) thick silt, sand, and clay veneer underlain by 40 feet (12.2 meters) of tight clay [2]. The majority of the lead contamination was limited to the thin soil veneer above the clay. The RD required the excavation, treatment, and disposal of soil containing a lead concentration exceeding 1,000 milligrams per kilogram (mg/kg) for the majority of areas at the site; however, the background lead concentration (220 mg/kg) was set as the cleanup standard for the acid disposal area. In this area, the potential for vertical lead migration was greatest based on the downward percolation of acidic liquids which may have mobilized lead. Sediment in an on-site ditch containing lead concentrations exceeding 450 mg/kg was also required to be excavated, treated and disposed.

The EPA mandated that the project be completed according to an arduous schedule, allowing the new project team only 17 months after privatization to complete the construction. Given the schedule, changes in the scope of the remedy were not welcomed by the EPA. Anticipating possible difficulties in meeting the required completion date, the EPA would not accept any deviation from the ROD, which would potentially trigger a lengthy public comment period. All potentially applicable cost reduction strategies were therefore required to meet the intent of the ROD without necessitating project delays.

VALUE ENGINEERING EFFORTS

Value engineering is a technical discipline that has been given a variety of definitions and meanings. The American Association of Cost Engineers (AACE) defines value engineering as:

“... a multi-discipline, systematic, and proactive function that is targeted at the design itself. The objective is to ... develop a facility or item design that will yield the least life-cycle costs or provide the greatest value while also meeting all functional, safety, quality, operability, maintainability, durability, and other criteria established for it.”

AACE also notes the important distinction between value engineering and other design activities such as design review and quality control [3].

With respect to the construction phase of the project life-cycle, Dell 'Isola [4] defines value engineering as:

“... a creative, organized approach whose objective is to optimize cost and/or performance of a facility or system ... It is concerned with elimination or modification of anything that adds cost to an item without contributing to its required functions.”

When the project was privatized, the United States Army Corps of Engineers (Corps) had completed 90 percent of the RD for the site. Based on its design, the Corps estimated that construction costs would be approximately \$13 million to which the EPA assumed oversight and engineering would add almost \$3 million for a total project cost of nearly \$16 million. At this point in the project, the Corps commissioned a formal value engineering study [5] to “... identify candidate options for fulfilling the general intent of the ROD objectives.” The Corps' value engineering study consisted of five phases [6] according to the work plan endorsed by the Society of American Value Engineers (SAVE) and the Corps. The five phases of the value engineering study were:

- The Information Phase during which the project reviewers were briefed on pertinent aspects of the site and the objectives of the study. Aspects of the remedial design that offered the greatest opportunity for cost savings were identified.
- The Creative Phase during which the project reviewers developed ideas and alternatives for modifying the design. Judgement on the merit of these ideas and alternatives were reserved until the next phase.
- The Analysis Phase during which the ideas for modifying the design were screened to eliminate those that were obviously “unacceptable.” The relative advantages and disadvantages of the surviving alternatives were identified. From this evaluation, a final list of the most promising concepts was compiled for detailed analysis.
- The Development Phase during which the life cycle costs were calculated for each alternative.
- The Presentation Phase during which the project review team presented the findings of the study to the decision maker. This was accomplished by conducting an “implementation meeting” following review of the draft study report.

The proposals considered during the value engineering study encompassed various aspects of the Corps' design. Some of the proposals involved minor changes with potential savings of less than \$25,000. Other proposals addressed contaminated soil handling methods and backfilling procedures. These proposals involved potential savings in the \$175,000 to \$190,000 range.

The most significant proposals considered in the value engineering study involved the means by which the treated soil would be disposed. Both the ROD and the Corps design required disposal of the stabilized soil in an off-site landfill. The value engineering study considered proposals for on-site containment using either a soil cover or a newly constructed waste cell, which were rejected. The potential savings associated with these proposals were \$4.1 and \$2.5 million, respectively.

Only two of the proposals from the value engineering study were accepted for implementation. The two proposals that were accepted represented less than three percent of the \$13 million construction cost estimated by the Corps. The three proposals offering the greatest opportunities to reduce project costs were rejected. The proposal that offered the best protectiveness and cost advantage was the constructed on-site

waste cell. This proposal represented a potential cost savings of \$2.5 million, 19 percent less than the \$13 million project cost estimate. The decision to reject this proposal was based on a combination of potential technical implementability difficulties and perceived administrative conflicts, especially permitting and scheduling problems.

VALUE-ADDED APPROACHES

Following privatization, the new project team re-evaluated the ideas identified in the value engineering study and developed several new approaches for improving the project and reducing implementation costs. While this work drew on some of the ideas contained in the formal value engineering study, it was more oriented towards an informal features/benefits analysis based on the remedy concepts and desired results. In this analysis, features which potentially improved, the project, were identified along with the resultant benefits. Benefits related not only to cost, but also included non-cost related advantages such as increasing the level of human health or environmental protection afforded by the project.

The techniques for adding value to the project which were considered included increased efficiency in construction sequencing, elimination of redundancies in construction and verification activities, modifications to the on-site stabilization approach, improvements in decontamination procedures, and alternative disposal options. Two of these features are discussed below. The first feature described was not considered during the value engineering study and was an alternative approach for verifying that the cleanup standards for the site had been achieved. It was successfully implemented with a resultant savings of about \$500,000. The second feature discussed below was previously evaluated and rejected during the value engineering study. This feature involved on-site containment of the stabilized soil rather than off-site landfilling as required by the ROD and the Corps' design. This option was rejected by the EPA a second time, not on the basis of technical implementability, but rather due to perceived administrative hurdles.

Soil Quality Verification

Value-added modifications in soil quality verification succeeded in optimizing the cleanup. Through alternatively conducting the excavation and verification phases of work, both time and expense were minimized. This alternative strategy was not addressed in the formal Value Engineering Study commissioned by the Corps, but was negotiated by the privatizing project team with the EPA.

The original excavation contours specified in the Corps' design sought to meet cleanup standards based on soil boring information collected during the remedial investigation. The minimum planned excavation depth was one foot (0.3 meters) near the site perimeter where fugitive contaminated dust was deposited. The maximum planned excavation depth was not specified, but was assumed to approach 15 feet (4.6 meters), approximately 11 feet (3.4 meters) below the top of the clay in the acid disposal area. The Corps' design also specified a soil removal and verification strategy to ensure that cleanup standards were met in the soil that remained in-place following excavation. The Corps' approach required excavation of soils to the specified depths, followed by initial soil sampling in grids to determine if additional excavation was required. The process was iterative until it could be demonstrated that the cleanup standard had been met.

The Corps' design also required that a portable X-ray fluorescence (XRF) instrument be used in the field to measure the total lead concentration in soil. The use of this instrument was intended to be the method for verifying that cleanup

standards were met. Laboratory data were to be statistically correlated to XRF data as a means of assuring the quality of the field instrument data. The quality assurance procedure, as specified in the Corps' design, was also iterative. An initial round of samples was to be collected and analyzed in a laboratory. The number of samples collected was to be statistically evaluated based on the variance of lead concentrations to determine if a representative number of samples had been collected. If not, additional samples were to be obtained until the number of samples representing a statistically valid population had been collected. After data from the appropriate number of samples had been generated, it was to be statistically correlated to the XRF data to verify that cleanup standards, as measured with the XRF, had been met.

This procedure contained a number of inefficiencies and redundancies, which would have required extensive time and expense to complete. The verification strategy would have been labor and capital intensive including iterative sampling, analytical, and statistical tasks. The portable XRF, an effective diagnostic tool, was superfluous in this approach considering the analytical verification requirement.

The project team identified an alternative approach as a value-added means of avoiding the inefficiencies in verifying that site cleanup standards had been satisfied. The alternative strategy was based on the geochemical interactions between lead and the soil and the effectiveness of the XRF instrument in saving time and financial resources by eliminating labor and iterative tasks. The alternative soil verification strategy, accepted by the EPA, included excavation to clay or to a depth which showed minimal visual evidence of contamination, *in-situ* XRF screening, followed by laboratory confirmation.

At the first disappearance of visible contamination or the first appearance of clay, which usually occurred at depths shallower than originally specified by the Corps' design, the XRF instrument was used to estimate the amount of lead remaining in the soil. When the cleanup standard appeared to have been met according to XRF data, 10 soil aliquots per sampling grid were obtained and composited into one sample for laboratory analysis. The XRF results were consistently within approximately 10% of laboratory analytical results for lead concentrations between 10^2 and 10^3 mg/kg.

Using the XRF as a screening instrument dramatically reduced sampling and analytical effort. Since lead tends to adsorb to soil particles, the clay interface served as a migration barrier. Screening the excavations based on physical conditions rather than excavating to the depths specified in the Corps' design eliminated approximately 5,000 cubic yards (3800 cubic meters) of soil from the excavation, treatment, and disposal process. Some areas originally planned for excavation were not excavated based on the results of the XRF data which were confirmed in the laboratory.

During the completion of the remedy, the shallowest actual excavation was six inches and the deepest was four feet. The elimination of excess soil from the remedial program reduced project costs without compromising the overall project objectives. The verification strategy saved time and money over that originally specified in the design and met the cleanup requirements.

This alternative verification strategy was not addressed in the value engineering study commissioned by the Corps and the benefits of its implementation would not have been achieved had the value-added approach not been applied. Through a features/benefit analysis, alternative approaches provided a remedy, unequivocally supported by field and analytical data faster and for lower costs.

On-Site Containment of Stabilized Soil

The second approach for adding value considered after privatization of the project included containment of the stabi-

lized soil in a newly constructed on-site waste cell. This approach would have replaced the off-site landfill disposal required in the ROD and the Corps' design. During the value engineering study, it was concluded that implementation of the on-site containment approach would result in a savings of approximately \$2.5 million. However, it was dismissed in the value engineering study as "institutionally difficult."

Disregarding the significant cost saving opportunities offered by the on-site containment approach, the government project team decided during the Presentation Phase of the value engineering study to reject this proposal as a candidate for implementation. The decision to reject on-site containment was based on "poor implementability." Specifically, the ability to obtain approvals needed for on-site construction was considered unknown. The value engineering study suggested that the time needed to obtain the required approvals was the most important disadvantage perceived by the EPA and resulted in proposal rejection.

Despite the decision on this approach, on-site containment of the stabilized soil was further pursued following privatization because the potential cost savings that could be realized under this approach were too significant to be ignored due to "institutional difficulties." On-site containment was re-evaluated with respect to all of the evaluation criteria that the EPA considered during a feasibility study. The re-evaluation considered how on-site containment would provide overall protection of human health and the environment, and whether it would comply with all pertinent regulatory requirements.

The long- and short-term effectiveness of on-site containment were also reviewed. As a result, it was determined that on-site containment posed fewer risks to human health and the environment than off-site disposal. Over the long-term, on-site containment would have been superior to off-site landfilling due to the reduced potential for degradation of the stabilized soils and resolubilization of the lead. Additionally, the on-site containment cell offered an improved ability to monitor the integrity of the containment system.

Since the initial decision to reject this approach was founded on perceived schedule concerns, the new project team scrutinized technical and administrative implementability in detail. Regulatory authorities that would be asked to grant approval for an on-site containment cell were contacted to inquire about their initial reaction and to gauge the timeframe required for obtaining those approvals. Technical concerns about the availability of adequate space to construct the on-site containment cell were evaluated by preparing a conceptual design for the cell. It was concluded that all of the administrative concerns could have been averted with conscientious project scheduling and coordination with the appropriate authorities. The technical implementability concern over the availability of adequate space could easily have been overcome through careful design.

The results of the evaluation were compared with a similar detailed evaluation of the off-site landfilling approach required by the ROD. The re-evaluation was submitted to the EPA for reconsideration. Again, the EPA did not accept the on-site containment cell approach despite the significantly lower costs, superior long-term performance, and reduced potential for adverse affects during the implementation period.

The opportunity to implement the value-added approach for on-site containment of the stabilized soil was denied because of the EPA concerns over the project schedule. The EPA's final rejection of this approach resulted from the perceived schedule delays associated with obtaining the necessary approvals to enable construction of the on-site waste cell. If the on-site containment approach had been aggressively pursued before the EPA established a firm construction completion date, it would have had a much greater chance of acceptance federally and locally.

Even though the value-added feature of on-site containment was blocked, the other methods of adding value to the project succeeded. The overall value-added approach ultimately yielded significant cost savings while improving remedial performance. Thus, the strategy of identifying and capitalizing on opportunities to add value at any point in the project while achieving the desired results was shown to be effective.

CONCLUSIONS

Based on the experiences gained during the remedial design and construction activities at the C&R Battery Company site, a number of limitations attributable to over reliance on the effectiveness of value engineering studies became evident. At the same time, adoption and conscientious application of a value-added approach to improve project outcome, in spite of the late point at which it was applied in the project, yielded significant cost and performance benefits.

The primary limitation of the formal value engineering study is that it is possible it may be overemphasized as a value-adding device and it may not be completed until late in the design stage at which point many fundamental and potentially costly decisions have been made. A value engineering study applied at the 90 percent completion point in the design, as evidenced herein, can result in lost opportunities to redirect the outcome of the project. Because of the timing, the most important decisions affecting approach and cost had long since been "cast in stone" [7] in the minds of many of the concerned parties. At this late stage, the modification opportunities are generally limited to minor design changes and have only minimal impact on project strategy and outcome due to increasing commitments to and consequences of the existing design.

The value-added approach to project execution differs fundamentally from the formal value engineering study approach. A value-added approach encompasses design modifications during the design phase, but it also encourages re-evaluation of the basic concepts of the project throughout the life of the project. The basic concepts, like on-site versus off-site materials disposal, offer the greatest opportunities for saving costs, improving performance, and yielding direct, tangible benefits to all parties involved. The primary advantage of the value-added strategy versus reliance on a formal value engineering study to improve overall project performance and minimize costs is that it promotes flexibility and a continued rethinking of project direction and desired results. Regardless of the level of completion of an on-going project, there are usually opportunities to capture significant cost and performance benefits by adopting a value-added mindset.

The benefits that can be realized by adopting a value-added approach can differ markedly depending on which party is controlling the project. This is probably due to different motivations among the project participants. While the C&R Battery project was federally-led, primary motivations appeared to be completion within a specified timeframe and public and environmental protection. During this stage, cost savings seemed to be subordinate to schedule compliance. Following privatization, schedule compliance and protection of human health and the environment remained primary motivational factors; however, preservation of financial resources became an important consideration. The cumulative result of all of the value-added enhancements following privatization yielded the desired, protective remedy ahead of schedule with a total cost savings of \$10 million from the EPA estimated \$16 million project cost.

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Reduction of Effluent Toxicity for a Printed Circuit Board Facility

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Resulting from 1987 modifications of the Clean Water Act, whole effluent toxicity became a new parameter for numerous NPDES discharges. Recently, a Connecticut printed circuit board manufacturer undertook whole effluent toxicity testing and subsequently, an effluent Toxicity Identification and Reduction Evaluation (TI/RE). The TI/RE consisted of parallel efforts to eliminate or reduce the sources of effluent toxicity to a vertebrate and an invertebrate species.

Testing showed that effluent toxicity to the fathead minnow, Pimephales promelas, and the daphnid, Daphnia pulex, was due to different causes. The primary toxicant identified in fathead minnow testing was shown to be unionized ammonia, generated primarily from circuit board etchant rinse processes. The primary toxicant in daphnid testing was shown to be an organic surfactant/defoamer used in the resist strip process. Efforts to identify the organic surfactant were successful and resulted in the isolation of a phosphate ester as the primary cause of toxicity to the daphnids. Product substitution was easily accomplished and resulted in marked reduction of effluent toxicity to Daphnia pulex. To reduce effluent ammonia toxicity, etchant rinse ammonia loadings will be reduced or eliminated from the process. The ammonia reduction program is discussed. Attainment of 'toxicity permit limits' will be achieved with use of pollution prevention/waste minimization techniques and without the need for additional facility waste treatment processes.

INTRODUCTION

Resulting from amendments to the Clean Water Act in 1987, NPDES dischargers were required to undertake biomonitoring, exposing wastewater effluents to indicator species to measure the toxicity of the effluent in a

laboratory-controlled setting. The biomonitoring of effluent is designed to eliminate toxic substances from reaching toxic levels in receiving streams.

A southern Connecticut printed circuit board manufacturer (PCM), one of the largest such facilities in the United States, undertook scheduled biomonitoring commencing in

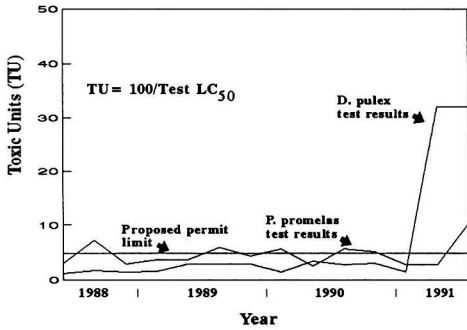


FIGURE 1. PCM facility, effluent biomonitoring results 1988–1991.

the third quarter, 1987. Typically, quarterly biomonitoring consisted of static, acute testing with the daphnid, *Daphnia pulex*, and the fathead minnow, *Pimephales promelas*. Effluent bioassay results were generally consistent over a 14-quarter period until 1991. The LC_{50} is commonly used to indicate the percent of effluent in the test solution where 50% of the test species die in forty eight to ninety six hours of exposure. *Daphnia* LC_{50} results ranged from 10 to 60 percent effluent. Fathead minnow LC_{50} results ranged from 10 to 60 percent effluent. A graphical representation of quarterly biomonitoring results during this time period is shown in Figure 1. Figure 1 presents effluent toxicity in Toxic Units (TU) where TU is the ratio of 100 and the test LC_{50} . Use of TU's allows positive correlation between test results and effluent toxicity.

The plant effluent flow ranged from 250 to 350 gallons per minute (gpm) and discharged to a small tidal creek, a tributary to a larger estuarine river. At the point of discharge, there was essentially no available dilution. Therefore, a proposed permit limit of a no observable acute effect level (NOAEL) of 100 percent effluent was developed. Both the small tributary and larger tidal river were predominantly fresh at this point with salinities at lowest flows ranging from zero to ten parts per thousand.

The facility manufactures multi-layer printed circuit boards for the automotive and computer industries. Use of an ammoniacal-etch process as well as other minor uses of ammonia in tin-strip and solder-brite processes yielded effluent ammonia concentrations which ranged from 50 to 100 mg/l. Wastewater treatment included no processes to reduce ammonia in the final effluent. Using a modified hydroxide/sulfide precipitation technique, the effluent metals values were consistently low, most often below 0.25 mg/l. Sufficient EDTA, discharged from electroless processes, appear to chelate metals which remain in the effluent after treatment.

The facility entered into a toxicity identification and reduction evaluation (TI/RE) in an effort consistent with other facility-wide upgrades. Numerous waste minimization and pollution prevention upgrades were being evaluated and implemented during this timeframe. It was evident that permit toxicological limits would be difficult or impossible to consistently meet at the existent discharge location. Therefore, the discharge was relocated to the larger estuarine system after dye dilution efforts were undertaken to ascertain the near-field mixing zone in this river system.

Coincidentally, commencing in the first quarter of 1991, *Daphnia pulex* biomonitoring results deteriorated markedly. Several successive testing events yielded LC_{50} values for the daphnid of less than 10 percent effluent ($> 10TU$). Even with the larger mixing zone afforded the facility with the relocation of its discharge, these results would not meet proposed permit limits. Fathead minnow biomonitoring results during

this timeframe did not deviate from consistent historical results. A proposed permit limit of an LC_{50} value greater than 20 percent effluent was promulgated by the Connecticut Department of Environmental Protection. Thus, the goals of the toxicity identification and reduction evaluation were defined. These were:

1. To demonstrate that un-ionized ammonia was the primary toxicant to the fathead minnow, *Pimephales promelas*, and
2. To determine primary and secondary toxicants to the daphnid, *Daphnia pulex*, using EPA Phase I toxicity identification protocol.

METHODS

EPA Phase 1 toxicity characterization procedures [1] were used to isolate ammonia as the toxicant to the fathead minnow. In January, 1990, EPA Phase 1 characterizations were performed on the effluent using fathead minnows as the test species. Subsequently, after project re-initiation, three modified EPA Phase 1 characterization procedures were performed using composited whole effluent from the PCM facility. This modified procedure, consistent with toxicity characterization procedures detailed in chronic toxicity identification and reduction evaluations [2], was designed to determine whether any toxicants were "masked" by others and whether elimination of primary toxicants (i.e., ammonia) resulted in effluent toxicity, to a lesser extent, due to a secondary toxicant. A test flow diagram of these two procedures appears in Figure 2.

A similar test series protocol was used for determining the toxicant(s) to the daphnid, *Daphnia pulex*. Slightly different test series were used in 1991 testing as different toxicants were suspected (Figure 2). The goal of toxicity characterization testing was to isolate toxicity in the effluent in a specific treated fraction, if possible, and to allow subsequent determinations, consistent with EPA Phase 2 toxicity identification testing [3], to be undertaken to allow identification of primary and secondary toxicants.

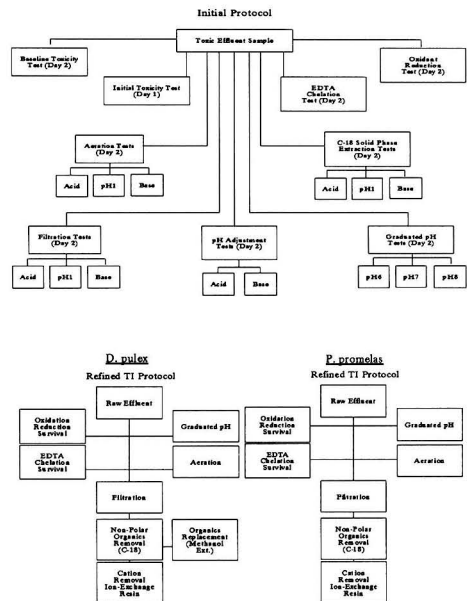


FIGURE 2. PCM facility, TI characterization, EPA test protocol.

Upon finding that much of the effluent toxicity to the daphnid was removed in C-18 resin filtration, various methods were used to extract the suspect non-polar organic from the C-18 resin. Use of a two percent methanol solution, consistent with EPA protocol, was not successful in extracting the toxicant. Therefore, chemical confirmation of the toxicant was undertaken in a different and more inventive manner.

Several C-18 resin samples were submitted to the chemical laboratory for digestion with methylene chloride. The resultant digestion dissolved both the toxicant which had been absorbed onto the resin as well as part of the C-18 resin. Chemical testing of the methylene chloride/resin sample was undertaken using a GC-MS scan which cross-referenced available chemical reference libraries and identified the 10 highest peaks. Results of initial and subsequent C-18 resin digestions were compared with material safety data sheets (MSDS) from the PCB facility for potential identification of a material found in chemical analyses and used in the PCB process chemistry.

RESULTS AND DISCUSSION

Initial effluent pH, due to metal precipitation processes ranged from 8.5–9.0. Two separate methodologies, pH reduction to pH 7.5 and 6 and cation exchange, reduced and/or eliminated effluent toxicity to the fathead minnow. Effluent ammonia analyses were performed upon receipt of the composite effluent sample. Additionally, “treated” ammonia and pH analyses were performed on manipulated samples after the Phase 1 manipulations detailed above.

The characterization procedures resulted in elimination of effluent toxicity to the fathead minnow upon pH adjustment to pH 6. In some cases, toxicity was eliminated upon adjustments to pH 7.5. Additionally, cation exchange resulted in reduced effluent ammonia concentrations with consistent reductions in effluent toxicity. Effluent un-ionized ammonia and initial (day 1) effluent toxicity (TU) showed a strong correlation.

Spiking the effluent with ammonia to 70 mg/liter on two separate occasions resulted in recreating the effluent toxicity to the fathead minnow at pH of 9.0 and eliminated it at a pH of 6.0. At a pH of 9.0, 28% of the ammonia is unionized, while at a pH of 6.0, the unionized ammonia is 0.04%. The development of the correlation between un-ionized ammonia and effluent toxicity to the fathead minnow and the recreation of toxicity with effluent ammonia spiking, achieved satisfactory confirmation of the toxicity of the effluent being due to effluent ammonia.

Toxicity characterization testing undertaken in 1990 with the daphnid, *Daphnia pulex*, showed similar toxicity trends to the fathead minnow. Effluent pH manipulation to pH 6 and pH 7.5 rendered the effluent non-toxic to daphnid. However,

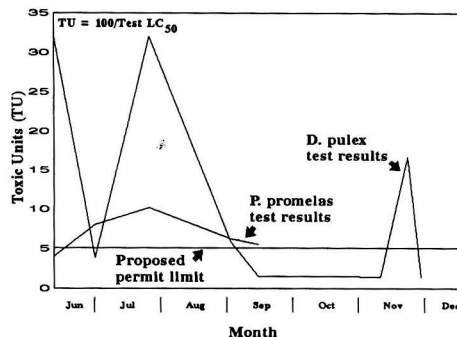


FIGURE 3. PCM facility, effluent biomonitoring results 6/91–12/91.

in 1991, biomonitoring results degraded dramatically. On several consecutive tests, effluent LC_{50} values were below 10 percent effluent ($> 10TU$). This trend continued through the remainder of toxicity characterization testing (Figure 3). The characterization methodology (Figure 2) was designed to develop a mass-balance of toxicity in the effluent and also to unmask toxicants which were hidden due to the presence of a more aggressive toxicant. Effluent fractionation for the daphnid consisted of one micron filtration, C-18 resin filtration, and a series of cation, anion and pH manipulations. On several occasions in toxicity characterization testing, C-18 filtration removed toxicity of the effluent to achieve an effluent LC_{50} of 40 to 80 percent effluent (2.5 to 1.25 TU). Some additional effluent toxicity was removed with pH manipulation. Effluent pH manipulation, by itself, did not alter effluent toxicity. Only through the layering of a series of effluent manipulations was the effluent rendered non-toxic following removal of the non-polar organic and subsequent effluent manipulations (Table 1).

Efforts to extract the C-18-removed organic from the resin were unsuccessful at first. The EPA methodology, to re-dissolve the adsorbed organic compound in a two percent methanol solution was unsuccessful. It did not recapture the effluent toxicity or yield the material in solution which could be measured using GC/MS Scan techniques. Subsequently, C-18 resin cartridges were forwarded to an analytical laboratory for methylene chloride digestion. A “top 10 peaks” GC-MS scan was performed on the resultant solution after digestion. It was evident, based upon investigation of chemical results, that the methylene chloride dissolved a portion of the resin. However, in all chemical analysis results, a phosphate ester (2-butoxy-ethanol phosphate) was shown to be present.

Investigation of process chemistry, which consists of over 200 separate products, many containing proprietary materials, showed the phosphate ester to match a defoamer used in

Table 1 PCM Facility TI Characterization Results

	6/5/91		9/2/91		
	D. pulex	P. promelas	D. pulex	P. promelas	
Initial Toxicity: Day 1	32	4.0	5.9	10.2	
Graduated pH:	pH 6.0	> 10	> 100	0.0	
	pH 7.5	> 10	32	1.6	
	pH 9.0	> 10	6.3	> 10	
	Filtration:	1 micron	> 10	—	—
	C-18	2.0	4.5	2.5	—
	C-18/Cation resin (series)	1.5	1.6	1.4	7.1

All units expressed as toxic units (TU).
TU = 100/Test LC_{50}

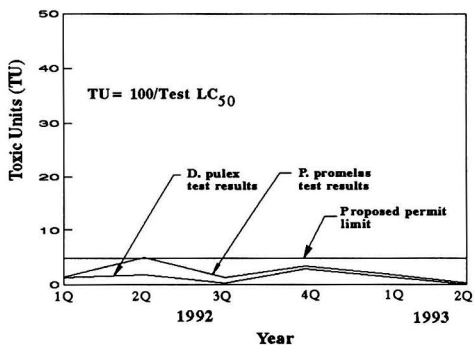


FIGURE 4. PCM facility, effluent biomonitoring results 1992-1993.

one process within the facility. Through investigation, it was determined that:

1. The defoamer was hand applied by manufacturing personnel to eliminate visible foam production from the resist strip process,
2. The rinse bath in the resist strip process had previously been maintained stagnant and shipped off site,
3. Commencing in early 1991, however, the rinse bath was batch-dumped periodically (every other day) to the waste treatment system, allowing the defoamer to be present in the wastewater.

Toxicity data of the phosphate ester in the literature could not be found. Pure compound testing using the daphnid, *Daphnia pulex*, showed an LC_{50} in the range of 25 to 35 mg/l when first dissolved in a solvent solution of 2% methanol. Using purchase records, which yielded a mass bought/used over time, and flow over the same time period, a calculated concentration of 30 to 35 mg/l was developed. However, use was not 'average', but rather intermittent with high dosages occurring occasionally and no dosages occurring over much of the time.

Spiking effluent samples with the pure compound, phosphate ester, resulted in matching the effluent toxicity of the effluent itself. Commencing in early 1992, the phosphate containing material was discontinued and a new defoamer brought into the resist strip process. This was done both for effluent toxicity concerns and as a precursor to initiation of a closed-loop resist strip installation using a prototype unit developed for testing on-site. The result of this substitution has been to bring the effluent into compliance with effluent toxicity limits as seen in Figure 4.

The ammonia concentration in the wastewater consisted of two distinct loads resulting from operation and cleanout processes. Cleanout was typically accomplished with a hydrochloric acid rinse of the tank bottoms on a weekly basis, and resulted in a highly concentrated acid copper ammonium chloride solution. Typically, the majority of the etch solutions are recycled to the etchant manufacturer. After discussions with the manufacturer, this acid copper ammonium chloride load was allowed to be mixed with the waste etchant and recycled to the manufacturing facility.

Evaluations were undertaken to minimize operational ammonia loads from the counter-current etchant rinse. While numerous pollution prevention options were developed in the concept, the one finally chosen was an ion exchange system which removed a very concentrated copper load from discharge to the industrial waste treatment facility (resulting in markedly less metal hydroxide sludge precipitation) and also removed ammonium in the cation exchange process. This pretreatment step went on-line in 1994.

Initial resin regeneration processes consists of sulfuric acid and the generation of an acid copper ammonium sulfate solution. However, evaluations will be undertaken to regenerate with hydrochloric acid and produce a regenerant solution which is recyclable into the etchant process. It is expected that by the end of 1994, ammonium concentrations from the facility will be reduced to a point where ammonia toxicity of the wastewater effluent to either of the species tested in the toxicity identification reduction evaluation will not exist.

CONCLUSION

An exhaustive study was performed to detail and quantify process chemical use at a PCM facility. Results of the toxicity identification evaluations undertaken as part of this effort showed the phosphate ester (2-butoxy-ethanol phosphate) to be the primary toxicant in the wastewater to the daphnid, *Daphnia pulex*. Secondly, effluent ammonia concentrations resulted in toxicity to daphnids. Unionized ammonia was also the primary toxicant to the fathead minnow, *Pimephales promelas*.

Product substitution and closed-looping the process resulted in the elimination of a defoamer used in a resist-strip bath from discharge to the waste treatment system at the PCM. Product substitution, and chemical recycle are the likely mechanisms which will be employed to reduce the ammonia discharge from the facility to the receiving stream. Facility-wide evaluations undertaken for the TI/RE have been useful in evaluating pollutant source and identifying numerous areas for further waste minimization efforts. An indication of the success of these efforts is reflected in recent flow data from the facility which, despite a 50% increase in production, has shown a minor reduction in flow during the time of that production increase. The facility has made great strides in achieving the goals of the 1987 amendments to the Clean Water Act by eliminating receiving stream toxicological impacts and setting an enviable record in waste minimization.

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Removal of Elemental Phosphorus from Electric Furnace Sludges of Various Origins

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A method developed by researchers at the University of Alabama has successfully eliminated the toxic and flammable characteristics of elemental phosphorous from by-product sludges produced from operations of electric furnaces at widely separated facilities. The removal process is first order with respect to elemental phosphorus concentration with a rate constant of 0.02 min^{-1} . The residuals produced contain cadmium, chromium, and lead concentrations above the TCLP limit and thus will require further treatment.

BACKGROUND

The electric furnace process, developed by TVA in the 1950's, is the most widely used technology for recovering white phosphorus from phosphate ores (Van Wazer, 1961). Typically, the furnace is charged with a mixture of phosphate nodules, silica, and coke. Baked-carbon electrodes are placed in the charge and an electric current is passed through the mixture. White phosphorus is formed and vaporized when the electrically heated charge reaches a temperature around 1400°C. The white phosphorus fumes are recovered by condensation with a water spray, which is at a temperature above the white phosphorus melting point. The white phosphorus liquid is separated from the water by gravity. An aqueous sludge by-product is produced that can contain significant amounts of white phosphorus, up to 40% of the solid phase. The ratio of water and sludge produced to white phosphorus recovered is about 5:1.

During the past half-century, there has been an accumulation of by-product sludge from the production of white phosphorus by the electric furnace process. At the peak production, 1.5 million metric tons of water and sludge were produced annually. These materials have been stored in holding ponds awaiting further treatment for recovery of the white phosphorus or its conversion to a non-hazardous form, such as a fertilizer. Storage of the by-product sludge has been in special containment ponds and vessels at 30 sites in 18 states. Figure 1 shows the location of these sites throughout the United States (EPA, 1971).

White phosphorus in the sludge poses two problems. Although sparingly soluble in water (3 ppm), it is toxic to aquatic

animals at concentrations well below its solubility limit. Discharge limits to surface waters have been proposed at 0.1 ppb (Gordon *et al.*, 1990). If the sludge containing white phosphorus is allowed to dry, the white phosphorus will spontaneously ignite. Thus the sludge is a potentially toxic and flammable hazard. Additional treatment is required before the sludge can be released to the environment.

Currently, the sludges are being treated by two methods; one requires screening to remove the larger white phosphorus particles; and the other converts the sludge to a fertilizer by chemical oxidation and neutralization (Edwards, 1993). The sludge from the screening process contains a few percent

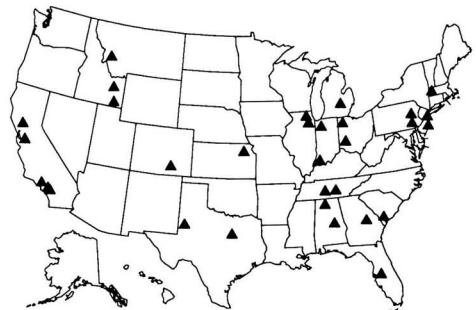


FIGURE 1. Locations of major contaminated elemental phosphorus plant sites (active and abandoned).

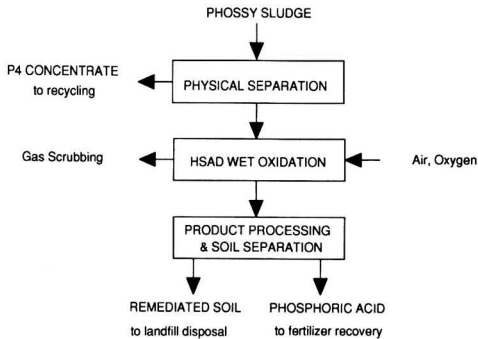


FIGURE 2. Flowsheet of the proposed soil remediation system.

of white phosphorus, which must be treated before final disposal. The high speed air dispersion (HSAD) treatment method described in this paper is applicable to the untreated and treated sludge.

EXPERIMENTAL

Sludges from white phosphorus plants in Alabama (TVA), Idaho (FMC), and Tennessee (Oxy) were supplied by plant personnel for this study. Approximately 20 gallons of sludge were provided by each site. These were considered to be representative of materials that require treatment.

Previous research (Anazia *et al.*, 1992) has shown that mechanical separation of the sludge can recover significant amounts of white phosphorus. For this reason, samples for testing were prepared by rough screening the sludge at 48 mesh. This simulates the production of an overflow material that is rich in white phosphorus and an underflow material that requires additional treatment to remove the residual phosphorus. The general scheme proposed for the treatment of the sludge is shown in Figure 2.

Samples for further study were prepared from the minus 48 mesh material by collecting 180 g samples while continuously stirring the sludge. A ladle was used to obtain the 180 g samples. The samples were stored in sealed, plastic containers until needed for the oxidation studies in the HSAD reactor.

Previous studies with the HSAD reactor (Jung, 1992) has shown that oxygen concentration, sludge concentration, and agitation intensity were the most important control variables. The other variables considered were air flow rate, pH, and temperature. As long as the sludge temperature was above 43°C, temperature was not a significant variable. All six variables were correlated by a non-linear, multi-variable regression program. Jung focused on the formation of oxyphosphorous compounds in the reactor. Three distinct periods were reported: an induction period, a rapid oxidation or reaction rate period, and a declining rate period. During the rapid reaction rate period, the reaction was zero order. Based on Jung's work, three levels of each of the most important variables were used in this research. Oxygen concentrations were 20%, 50%, and 80%; sludge concentrations were 3.75 wt%, 7.5 wt%, and 15 wt%; agitation intensities were 4000 rpm, 6000 rpm, and 8000 rpm.

A schematic diagram of the HSAD reactor is shown in Figure 3. The reactor depends on a high speed mixer to produce microbubbles of air that react rapidly with the elemental phosphorous in the sludge. A complete description of the reactor has been given previously (Jung, 1992 and Hanna and Jung, 1992).

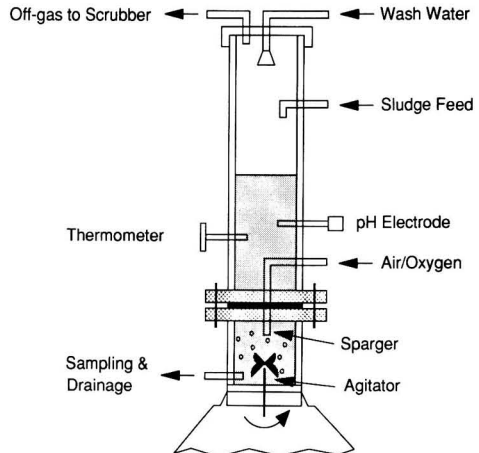


FIGURE 3. HSAD column reactor schematic.

The reactor was charged with about 750 mL of tap water and the proper airflow established. The correct amount of sludge was then added, the agitator started, and a sample taken. The speed of the agitator was set to the desired level by using an optical tachometer. Samples were taken every 15 minutes during the reaction. When the evolution of white fumes (P_2O_5) ceased, agitation was continued for 30 minutes. The cessation of white fumes marked the end of what Jung had described as the rapid oxidation stage. Although this stage usually lasted less than an hour, sampling continued for up to 3 hours of reaction time.

RESULTS AND DISCUSSION

The chemical characteristics of the various sludges as received are shown in Table 1. Analyses were performed with

Table 1 Chemical Characteristics of P_4 Sludges from FMC, TVA, and OXY

	FMC, ppm		TVA, ppm		OXY, ppm	
	Solid	Aqueous	Solid	Aqueous	Solid	Aqueous
P_4	44,000	ND	34,000	200	35,000	190
Metals						
Ca	13,500	61	12,250	9,600	10,400	253
Cd	730	0.13	47.5	527	7.6	0.023
Cr	40	0.04	52.5	150	19.0	0.083
Cu	30	0.09	247.5	15	36.3	0.035
Mg	580	28.5	650	6,000	222	32.3
Pb	110	0.3	785	100	227	0.168
Zn	10,260	7.6	1,018	20,000	515	2.93
Anions						
Cl	970	1,485	ND	ND	ND	44.4
F	810	578	279	ND	ND	154.2
NO_2	ND	ND	ND	ND	ND	*
NO_3	ND	ND	8	ND	ND	31.2
PO_3	ND	ND	1,000	ND	ND	827
PO_4	31,580	2,961	5,600	ND	ND	4,110
SO_4	ND	240	30	ND	ND	79.2

ND—Not Determined, *—Not Detected

Table 2 Typical Chemical Analyses of the Sludge Aqueous Phase from TVA, FMC, and OXY

Constituent	TVA		FMC		OXY	
	Raw ppm	Reacted ppm	Raw ppm	Reacted ppm	Raw ppm	Reacted ppm
Cadmium	104	580	0.018	95	0.023	0.09
Calcium	7500	6400	8.54	2290	253	295
Chloride	ND	ND	59.5	174	44.4	*
Chromium	63	259	0.006	10.0	0.083	1.34
Copper	10	23	0.013	0.34	0.035	0.06
Fluoride	ND	ND	112	1750	154.2	93.0
Lead	7	379	0.312	18	0.168	2.0
Magnesium	7100	3100	3.99	310	32.3	10.4
Nitrate	ND	ND	ND	ND	31.2	*
Nitrite	ND	ND	ND	ND	*	*
Phosphate	2250	5630	1116	6440	2961	51000
Phosphite	300	1900	1645	2400	380	1160
Sulfate	ND	ND	52.9	150	79.2	53.8
Zinc	18400	20800	1.064	2275	2.93	25.1

ND-Not Determined, *-Not Detected

an ion chromatograph for anions, a gas chromatograph for elemental phosphorus, and atomic absorption for cations. Toluene extraction was used to recover the elemental phosphorus from the solid and aqueous phases. The variability of any single species in the sludges is from one to two orders of magnitude. All of the sludges are remarkably similar. The differences in aqueous phase metal analyses between the TVA sludge and the other two is probably due to the age of the sludge. The TVA sludge was collected from the bottom of a storage tank that had been idle for several years. The others were taken from active operations.

The after-treatment aqueous phase chemical analyses are given in Table 2. For comparison purposes, the untreated or raw water analyses are given also. Since the 180 g slurry sample is diluted to 1 L in the reactor, all of the reacted values reported have been corrected back to the same basis as the raw water.

The spent sludge solids from the reactor were tested for heavy metal concentrations that would exceed allowable levels. The TCLP analyses for the reacted solids are shown in Table 3. The highlighted values are those that exceed the allowable level for discharge to the environment. Of the three metals, lead exceeds the allowable in all but one of the materials tested. The low pH (less than 2) of the reaction aqueous phase is responsible for the excess amounts of heavy metals in solution. This suggests that precipitation by neutralization with a base would reduce the dissolved metals to an acceptable level.

Table 3 TCLP Analyses for Reacted Sludge Samples from TVA, FMC, and OXY

Constituent	TCLP Limit ppm	Reacted Solids ppm			Reacted Liquid ppm		
		TVA	FMC	OXY	TVA	FMC	OXY
Cadmium	1.0	0.04	47.0	0.67	2.5	67.0	0.41
Calcium	None	2.40	377	299	130	77.0	296
Chromium	5.0	0.04	3.0	2.32	1.40	12.0	1.34
Copper	None	0.70	9.0	0.78	65.0	7.0	0.06
Lead	5.0	0.22	8.0	6.50	24.0	30.0	5.38
Magnesium	None	0.66	9.0	7.13	25.0	185	10.8
Zinc	None	4.30	43.7	45.0	200	430	37.0

Table 4 Typical Elemental Phosphorus Analyses of Sludge Samples from TVA, FMC, and OXY

	Solid Residue ppm			Supernatant Solution ppm			Scrubber Solution ppm		
	TVA	FMC	OXY	TVA	FMC	OXY	TVA	FMC	OXY
Initial	34,000	44,000	35,000	200	160	1.9	-	-	-
Final	18	37	40	0.04	0.08	ND	ND	ND	ND

ND-Not Detected

The solids and liquid from the reactor were analyzed for their elemental phosphorus content with typical results shown in Table 4. The solids from the reactor do not exhibit any auto-ignition characteristics. Although the removal of elemental phosphorus from the supernatant solution has been greater than 99.9%, these levels are still toxic to aquatic animals. Additional dilution, extended reaction time, or additional treatment will be required before release to the environment.

The slight effect of agitation on the rate of phosphorus removal from the sludge is illustrated by Figures 4 and 5. Above 6000 rpm, there appears to be no difference in the rate of removal of elemental phosphorus; although the final phosphorus concentration is least at the 8000 rpm.

The effect of oxygen concentration on the rate of removal of phosphorus from the sludge is illustrated by Figure 6. Although the early slopes are nearly the same, the 80% oxygen removed the phosphorus to the lowest level. This behavior with Oxy sludge is similar to that observed with TVA and FMC sludges. Even at 20% oxygen, the concentration of oxygen in the sludge-air mixture is in excess of the stoichiometric

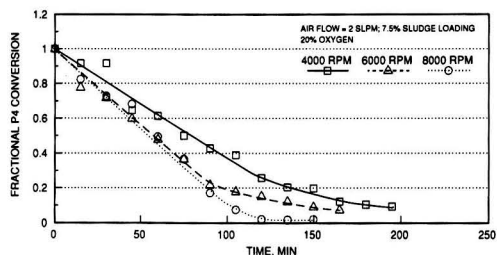


FIGURE 4. Conversion of TVA P_4 as a function of agitation.

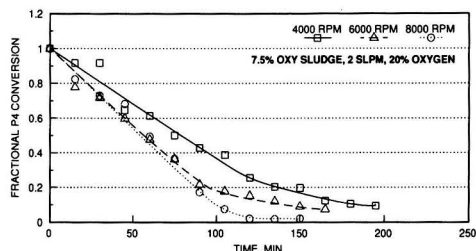


FIGURE 5. Conversion of OXY P_4 as a function of agitation.

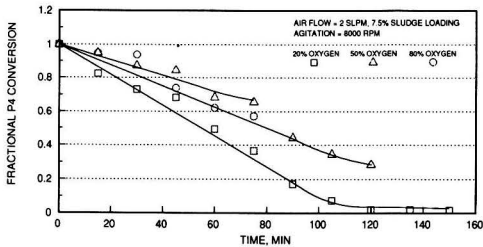


FIGURE 6. Effect of oxygen concentration on OXY P_4 removal.

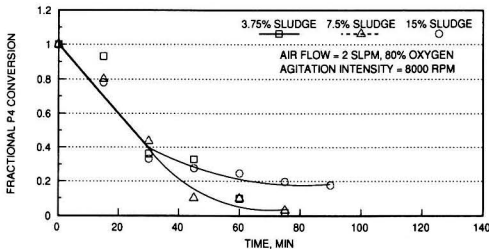


FIGURE 7. Effect of sludge loading on FMC P_4 removal rate.

amount required. Air would be the most economical and practical source of oxygen.

The effect of sludge loading on the removal rate of elemental phosphorus is shown in Figure 7 for FMC sludge. Typical of all three sludges studied, there is an initial constant rate then a declining rate.

The oxidation behavior of the three sludges are shown in Figure 8 for an air flow of 2 standard liters per minute (SLPM), an agitator speed of 8000 rpm, and an oxygen concentration of 80%. The curves shown are for a first-order reaction with respect to the elemental phosphorus concentration. The equations describing the removal rate are given by the following expressions:

OXY

$$[P_4]_t = [P_4]_o * \text{EXP}(-0.0152 * t)$$

TVA

$$[P_4]_t = [P_4]_o * \text{EXP}(-0.0196 * t)$$

FMC

$$[P_4]_t = [P_4]_o * \text{EXP}(-0.0217 * t)$$

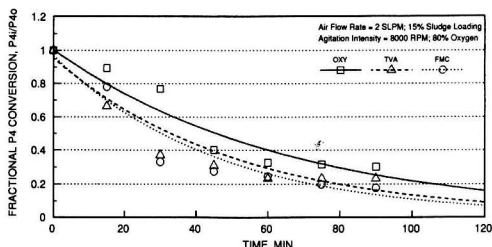


FIGURE 8. P_4 Oxidation rates for OXY, TVA, and FMC sludges.

The correlation coefficients for these equations are all greater than 0.9. When scatter in the data caused by the inherent sampling problems of a three phase system and the effect of temperature are considered, there appears to be no real differences among these equations or the oxidation behavior of the sludges. The first order rate constant for the removal of elemental phosphorus from these sludges is thus about 0.02 min^{-1} . All of these sludges are amenable to removal of their elemental phosphorus content by the HSAD wet oxidation process. A level is easily achieved where the sludge no longer exhibits toxicity or flammability from the elemental phosphorus content.

CONCLUSIONS

The chemical and physical characteristics of electric furnace sludges from different geographical locations have been studied. Each sludge was treated by oxidation with the HSAD process. All of them responded in a similar manner. Removal of the elemental phosphorus to non-toxic levels can be achieved in a few hours by the HSAD process. The treated solids and liquids may have to be treated for heavy metal removal before release to the environmental.

ACKNOWLEDGMENT

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Integration of Chemical and Biological Oxidation Processes for Water Treatment: Review and Recommendations

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The literature of studies which used a combination of chemical and biological degradation (usually oxidative) of organic contaminants in water is reviewed. Beneficial effects of such two-step treatments are commonly reported; these results, primarily from laboratory studies, suggest potential advantages for water treatment via process integration rather than single technology processing.

Four wastewater contaminant types are identified which can benefit from combined processes: 1.) recalcitrant compounds 2.) biodegradable wastes with small amounts of recalcitrant compounds 3.) inhibitory compounds and 4.) intermediate dead-end products. The design key for such two-step systems lies in choosing processes that complement each other and lead to a synergistic effect. Predicting this performance outcome requires knowledge of the physical, chemical and biological properties of the major reaction intermediates and their susceptibility to degradation by each process.

Economic, physical and technological limitations of the individual processes should be recognized for design of more effective and economical integrated processes. The ultimate treatment goal, whether specific pollutant removal or reduction of a global parameter such as TOC, must be known so that appropriate and complementary processes can be utilized. More work is needed concerning the degradation kinetics within the combined process, from initial attack of the primary compound through dynamics of intermediates and on to total mineralization.

INTRODUCTION

The development of "priority pollutant" lists and the increased continuing liability from wastewater effluents sent off-site have raised interest in destructive and oxidative processes for contaminant removal. Among the variety of physical, chemical and biological processes developed for water treatment, each has inherent limitations in applicability, ef-

fectiveness and cost. Physical processes such as precipitation, adsorption or air stripping, for example, transfer pollutants from the aqueous to a second phase, but the pollutant is not destroyed. Chemical oxidation may be slow to moderate in rate and selective, or rapid but non-selective, thus generating appreciable reactor or oxidant costs. Aerobic biological oxidation is limited when the feed is either recalcitrant to biodegradation, or inhibitory or toxic to the bioculture. Other

conversion processes may be limited by economics, oxidative potential, effluent characteristics or tendency to form harmful by-products. Effective treatment of a particular wastewater, given these limitations, may require a combination of available processes in such a way as to exploit their individual strengths and thus attain the desired water characteristics within reasonable economic constraints. Domestic wastewater treatment plants have long employed a wide range of physical, chemical and biological processes positioned to take advantage of each unit operation strength, exemplifying this approach.

Integration of destructive processes for recalcitrant or inhibitory contaminant conversion is advantageous conceptually. Wastewater that is toxic, inhibitory or refractory to biological cultures can be chemically pretreated to produce biogenic intermediates. Conversely, biological pretreatment can initially remove the biodegradable fraction of wastewater containing a mixture of refractory and biogenic compounds, and thereby conserve subsequent use of expensive chemical oxidant for the small remaining refractory fraction.

Despite extensive water treatment experience, surprisingly little basic engineering research has addressed the combining of chemical and biological processes and how this combination affects the global contaminant removal efficiency. Such information can be useful for optimizing pollutant removal and minimizing economic cost. Several studies have noted the change in biodegradability of a waste stream subjected to prior chemical oxidation [1, 2, 3, 4, 5, 6]. The approximately fifty studies of chemical and biological degradation processes in series have appeared only within the last twenty years, with much of the research activity occurring only very recently. We review this prior literature below. The increase in pollutant destruction that often accompanies such two-step process combination will be evaluated and key engineering elements and needs discussed.

PRIOR LITERATURE

Previous studies using some form of combined chemical oxidation and biological process to treat difficult contaminants in wastewaters appear in Table 1. This survey spans treatment problems ranging from contaminated groundwater to highly specialized industrial wastewater. The treatment objective varies with each study, as shown by the number of methods used to measure the biodegradability of the waste and eventually the removal effectiveness of the combined system. The chemical processes utilized include hydroxyl radical-mediated advanced oxidation processes, as well as ozone, hydrogen peroxide, permanganate and natural sunlight, among others. Biological processes include both aerobic and anaerobic pure and mixed cultures. The final column of Table 1 provides a qualitative measure of how the process combination influenced the effectiveness of the overall system compared to controls. This measure follows the conventions in Table 2. Combination of oxidative processes generally leads to increased degradation of the target compound(s) with some exceptions: Nine cases noted a dramatic increase (++) and all others reported a modest increase (+) for at least one pollutant.

Wastewaters Amenable to Combined Processes

Four types of wastewater are identified below that show potential for increased degradation by combined processes. The wastewater characteristics dictate the types below and often indicate the order in which the chemical and biological processes are applied. Most studies in Table 1 follow the expected sequential treatment order as described for each wastewater type, however two reports found success with cy-

cling of biological and chemical schemes [7, 8] while others examined concurrent oxidative treatments [9, 10, 11, 12]. The four types of wastewaters follow:

Type I. Recalcitrant Compounds

Large macromolecules such as soluble polymers may not be easily biodegradable due to their size or lack of reactive sites. Chemical oxidation can break these compounds into smaller, biodegradable fragments. Ultraviolet light photolysis [13] ozone [14, 15] photocatalysis [16] and ozone followed by hydrogen peroxide [17] have been used for this purpose. Biological degradation of the untreated contaminant was negligible for these examples. Chemical oxidation led to smaller chain lengths, increased biological activity and eventually greater degradation of the compounds. Suzuki *et al.* [17] found that polyethylene glycol needed to be broken down to a molecular weight of at most 300 before a bioculture could utilize it. Narkis and Schneider-Rotel [18] used ozone to degrade the surfactant nonyl phenol ethoxylate into smaller and more biodegradable compounds.

Other synthetic compounds are also recalcitrant and require chemical oxidation before significant biological activity can occur. Steber and Wierich [19] found that 1-hydroxyethane-1,1-diphosphonic acid (HEDP) could not be biodegraded without pretreatment with sunlight in the presence of photosensitizers. Kiwi *et al.* [20] found that treatment of recalcitrant anthraquinone-2-sulfonic acid sodium salt with Fenton's reagent (H_2O_2 with iron salts) led to a significant enhancement in biological activity. Kearney *et al.* studied the degradation of pesticides [21, 22, 23], herbicides [24] and recalcitrant munitions [25] by combined chemical and biological oxidation processes. Yocum *et al.* [26] ozonated industrial wastewaters from toluene diisocyanate, ethylene glycol, styrene monomer and ethylene dichloride production processes and found increased biodegradability due to the chemical pre-oxidation step. Adams and Spitzer [27] found that treatment of a number of finish oils and emulsifying agents (with the exception of ethoxylated alkylphenol) benefitted from ozone/hydrogen peroxide pretreatment.

Stable natural organic matter such as humic acids have also been subjected to combined processes [28, 29]. Chemical oxidation caused these macromolecules to release or fragment into smaller biodegradable compounds. Much of the earlier literature considering chemical oxidation followed by biodegradation was concerned with this effect in the detrimental sense that drinking water disinfected with ozone promoted subsequent biological growth in water distribution system [30, 31]. Currently, biological/sand filters following ozonation are routinely used to remove such biodegradable oxidation products [32]. Research with ozone followed by biologically active granular activated carbon (BAC) demonstrated that the combination can significantly influence water quality, with examples of either negative or positive results [33, 34, 35].

Type II. Largely Biodegradable but Requiring Subsequent Chemical Polish

Domestic and some industrial wastewaters contain large amounts of biodegradable organics in addition to relatively small concentrations of recalcitrant compounds. These latter, persistent compounds may lead to noncompliance in discharge effluent if not specifically removed. Combination of biological followed by chemical processes may prove useful in this situation. Biological treatment mineralizes the large biodegradable portion, effectively reducing the residual chemical oxygen demand of the water. A chemical polishing treatment is then applied to degrade the persistent com-

Table 1 Studies Utilizing Chemical and Biological Degradation of Organic Compounds

Authors	Chemicals Degraded	Concentration	Chemical Oxidation Scheme	Biological Degradation Scheme	Measure of Biodegradability	Order of Scheme	Grade*
Adams et al. 1993 (37)	1,4-dioxane, 2-methyl-1,3-dioxolane	2.3×10^{-3} M	UV/Ozone	Anaerobic pretreatment in some cases and aerobic post-treatment	BOD ₅ and removal of COD	B → C → B and C → B	+
Adams et al. 1994 (36)	1,4-dioxane, 2-methyl-1,3-dioxolane, 1,3-dioxolane	$2.2 - 2.6 \times 10^{-3}$ M 220 mg/L 220 mg/L	Ozone/Hydrogen Peroxide	Anaerobic pretreatment in some cases and aerobic post-treatment	BOD ₅ and removal of COD	B → C → B	+
Adams and Spitzer 1994 (27)	Finish Oils, Emulsifying Agents	1000 mg/L	Ozone/Hydrogen Peroxide	Activated Sludge culture	Removal of TOC	C → B	+ / 0 / -
Amador et al. 1989 (29)	Glycine-humic acid complexes	10 µg/ml	Artificial Sunlight Irradiation	Soil Microorganisms	Evolution of 14-CO ₂	C → B	+
Anagiotou et al. 1993 (8)	Domestic Landfill Leachate	5500-8800 mg/L COD	Fenton's Reagent	Activated Sludge	BOD ₅ , COD, measure of NH ₃	B → C → B and C → B	+
Barton and Drake 1994 (66)	Methanol, Reduced sulfur compounds, Turpenes (Blow heat condensates)	3950-5400 mg/L BOD ₅ to chemical reactor Diluted to 308 mg/L BOD ₅ to bioreactor	Fenton's Reagent	Activated Sludge culture in flow-through reactors	Dissolved oxygen concentration, mixed liquor settleability and soluble BOD ₅	C → B	+ / 0
Baxter and Sutherland 1984 (43)	2,4-dichlorobiphenyl	0.1-1 mg/50 ml bacterial suspension	Artificial Sunlight Irradiation	<i>Pseudomonas</i> isolated from Activated Sludge	Degradation of primary and intermediate compounds	B → C	+
Berge et al. 1994 (39)	Pulp and paper wastewater	18 mg/L AOX	Electron beam with and without oxygen and hydrogen peroxide	Activated Sludge culture	Removal of DOC and AOX Oxygen uptake	C → B	+ / 0
Bowers et al. 1989 (62)	2,4-dichlorophenol, Dinitro-o-cresol, Industrial Wastewaters	758 mg/L COD 335 mg/L COD 1277 and 6365 mg/L COD	Fenton's Reagent	Acclimated and non-acclimated Activated Sludge	Maximum specific substrate utilization rate	C → B	+ / 0
Bowers et al. 1991 (56)	Pyrrrolidine, Sulfanilic Acid, Naphthalene, Phthalic Acid, Diphenylamine, Skatole, Benzaldehyde, Indole, Catechol, Resorcinol, Hydroquinone, Vanillin, Pyrogallol, Salicylic Acid, Coumarin	5×10^{-3} M	Fenton's Reagent, Potassium Permanganate or Ozone	Activated Sludge culture	Removal percentage of COD Measurement of toxicity	C → B	+ / -
Brunet et al. 1982 (33)	Surface Water	Not explicitly given	Ozone	Biologically active granular activated carbon	Oxygen uptake Measurement of ATP and dehydrogenase activity	C → B	+

Carberry and Banzing 1991 (65)	Toluene, Trichloroethylene, Pentachlorophenol	4.7 x 10 ⁻⁴ M 5.5 x 10 ⁻⁴ M 1.0 x 10 ⁻⁴ M	Fenton's Reagent	Microbial cultures derived from contaminated soil	Michaelis-Menten rate constants	C → B	+ / 0
Cozzens and Adams 1994 (74)	2,4-dinitrophenol, 4-nitrophenol, 2,4-dichlorophenol, 4-chlorophenol, 4-aminophenol, 2,4-diaminophenol, 2-amino-4-nitrophenol, 2-amino-4-chlorophenol	30 mg/L and 200 mg/L	Ozone or Ozone/Hydrogen Peroxide	Activated Sludge culture	Removal of COD	C → B	+ / -
Eckstein 1994 (59)	Naphthalene, Phenanthrene, Pentachlorophenol	59 µM 4.35 µM 49 µM	Ozone/Hydrogen Peroxide	Specific degraders or Activated Sludge cultures	Evolution of 14-CO ₂ . Measurement of toxicity	C → B	+ / -
Gilbert 1987 (42)	Substituted Aromatics (28 compounds)	1 x 10 ⁻³ M	Ozone	Biological Oxygen Demand	Ratio of BOD ₅ /DOC as a function of percent COD reduction	C → B	+
Gilbert 1984 (69)	Aromatic Industrial Wastewater, EDTA-contaminated wastewater	1730-5300 mg/L COD 20 gram/L EDTA (11000 mg/L COD)	Fenton's Reagent	Activated Sludge	Ratio of BOD ₅ /COD and BOD ₂₀ /COD	C → B	++
Guillet et al. 1974 (13)	Polystyrene	Not explicitly given	UV-light	Soil microorganisms or Activated Sludge microorganisms	Evolution of 14-CO ₂	C → B	++
Hao et al. 1994 (73)	Dinitrotoluene Sulfonates (Red Water)	665 mg/l COD	Wet Air Oxidation	Activated Sludge culture, <i>Acinetobacter</i> or <i>Nitrosomonas</i>	Removal of COD Increase in biomass and nitrite production for the respective cultures	C → B	+ / 0
Hapeman et al. 1994 (44)	Atrazine	Not explicitly given	Ozone	Indigenous soil microorganisms, <i>Pseudomonas</i> (strain A) (PSA) or <i>Klebsiella terrigena</i> (strain DRS-1)	Removal of ozonation product	C → B	++
Heinzle et al. 1992 (7)	Chlorine bleaching effluents	≈ (1-2 g/L) COD	Ozone	Biofilm culture	Removal of TOC, COD, AOX	C → B, B → C, and cycling	+
Hu and Yu 1994 (63)	2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol	500 mg/L	Ozone	Acclimated and non- acclimated Activated Sludge	Removal of COD	C → B	+ / -
Hwang et al. 1986 (11)	4-Chlorophenol, 2,4-Dichlorophenol, Phenol, 2,4,5-Trichlorophenol, Pentachlorophenol	25 µg/L	Photolysis with natural sunlight	Natural microbial population	Evolution of 14-CO ₂	C + B	+

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Janssens et al. 1984 (34)	Water Treatment filtrate	2.0-3.7 mg/L TOC	Ozone	Biologically active activated carbon filtration	Removal of Assimilable Organic Carbon (AOC) Specific oxygen demand	C → B	+
Jones et al. 1985 (54)	Oil shale wastewater (Previously subjected to biooxidation)	1500-1800 mg/l DOC	UV-light, Ozone or Ozone/UV	Aerated acclimated microorganisms	Removal of Dissolved Organic Carbon (DOC)	C → B	++
Katayama and Matsumura 1991 (9)	PCB, TNT, TCB, TCDD, DDT and others	1 µg/mL	UV-light	UV resistant White rot fungi (<i>P. chrysosporium</i> BKM F-1767)	Evolution of 14-CO ₂	C + B	+
Kearney et al. 1986 (21)	Coumaphos	1500 mg/L	UV/Ozone	<i>Fluorobacterium</i> sp. ATCC 27551 suspension and also soil columns	Evolution of 14-CO ₂ Degradation of parent compound	B → C → B	+
Kearney et al. 1988 (22)	Atrazine	33 mg/L 100 mg/L	Ozone (pH 6.5, 8 10)	Soil Microorganisms or soil microorganisms with <i>Pseudomonas</i> sp. strain A	Evolution of 14-CO ₂	C → B	+
Kearney et al. 1983 (25)	Trinitrotoluene (TNT)	1 or 10 mg/L	UV/Ozone	Soil Microorganisms and <i>Pseudomonas Putida</i> in biometer flasks	Evolution of 14-CO ₂	C → B	+
Kiwi et al. 1993 (20)	Antraquinone Sulfonate	3 x 10 ⁻³ M	Photo-assisted Fenton's Reagent	Incubation with sewage sludge	Zahn-Wellens biodegradability test	C → B	+
Kong and Saylor 1983 (12)	4-chlorobiphenyl	0.7 mg/L	Artificial Sunlight Irradiation	Incubation by mixed culture obtained from river sediment	Evolution of 14-CO ₂	C → B	+
Koyama et al. 1994 (64)	Chlorobenzoates, monochlorophenols, dichlorophenols, p-dichlorobiphenyl	53 - 3876 µM	Fenton's Reagent	Methanogenic Digester Sludge	Removal of TOC Evolution of methane	C → B	+
Langlais et al. 1989 (14)	Paranitroaniline, P.E.C. (M.W. 8000), Anthraquinone-2-sulfonic acid	7.2 x 10 ⁻⁴ M 3.05 x 10 ⁻⁴ M 1.25 x 10 ⁻⁵ M	Ozone	Activated Sludge microorganisms on biodisks	Carbon elimination flux Ratio of BOD ₅ /TOC	C → B	++/0
Lee and Carberry 1992 (53)	Pentachlorophenol	1 x 10 ⁻³ M	Fenton's Reagent or Hydrogen Peroxide	Selected Microbial Consortium (<i>Pseudomonas putida</i> and <i>Pseudomonas aeruginosa</i>) and Activated Sludge	Oxygen uptake to determine kinetic rate constants, Degradation of primary compound Removal of COD	C → B	+
Manuil et al. 1992 (41)	2,4-dichlorophenol, Pentachlorophenol, Methyl vinyl ketone	75 mg/L 75 mg/L 75 mg/L	TiO ₂ /Sunlight	Activated Sludge	Respiration rates compared to nontoxic controls to determine inhibition	C → B	+
Medley and Stover 1983 (78)	Acrylonitrile, 1,2-dichloropropane, 2,4-dinitrophenol	100 mg/L 100 mg/L 200 mg/L	Ozone	BOD using acclimated and nonacclimated seeds	Ratio of BOD ₂₀ /TOC and BOD ₂₀ /COD	C → B	+/-

Miller et al. 1988 (61)	Benzo [a] pyrene	100 mg/L	UV light or natural sunlight with and without Hydrogen Peroxide	Incubation with Activated Sludge or soil test system	Evolution of 14-CO ₂	C → B	+
Miller et al. 1988 (60)	2,4-dichlorophenol, 2,4,5-trichlorophenol	100 µg/mL	UV light with and without Hydrogen Peroxide	Incubation with Activated Sludge or soil test system	Evolution of 14-CO ₂	C → B	++
Narkis and Schneider-Rotel 1980 (18)	Nonyl phenol ethoxylate	≈ 40 mg/L	Ozone	Incubation for 20 days with sewage sludge (Modified OECD method)	Removal of COD and TOC Ratio of COD/COD ₀ and TOC/TOC ₀	C → B	+
Narkis and Schneider-Rotel 1980 (67)	Municipal Waste, Municipal + Industrial Waste	24-160 mg/L COD	Ozone	Activated Sludge microorganisms	BOD ₂₀ and Ratio of COD/COD ₀ and TOC/TOC ₀	C → B	+
Ravikumar and Gurol 1991 (10)	Pentachlorophenol	1 M	Fenton's Reagent	Mixed culture in soil columns	Heterotrophic plate counts	C + B	+
Sierka and Bryant 1994 (40)	E-stage wastewater	1000 mg/L TOC	TiO ₂ /Sunlight (with and without ozone) and ultrafiltration	Activated Sludge culture	Removal of COD, TOC, AOX and color Measurement of toxicity	C → B	+
Somich et al. 1990 (23)	Metolachlor, Atrazine, Cyanazine	1- 100 mg/L range	Ozone/Hydrogen Peroxide	Soil metabolism	Evolution of 14-CO ₂	C → B	++/+
Somich et al. 1988 (24)	Alachlor	100 or 240 mg/L	Ozone or UV-light	Soil metabolism	Evolution of 14-CO ₂	C → B	++
Speitel et al. 1993 (72)	Precursors of trihalomethanes and haloacetic acids	2.3-3.3 mg/L TOC	Ozone	Biofilm	Removal of TOC and TTHMPF (Total trihalomethane formation potential)	C → B	+ / 0
Steber and Wierich 1986 (19)	1-Hydroxyethane - 1,1 - diphosphic acid (HEDP)	0.2-0.14 mg/L	Artificial or Natural Sunlight	Anaerobic incubation by sewage sludge and also green algae	Evolution of 14-CO ₂	C → B	++
Stowell et al. 1992 (70)	2-chlorophenol	1.43 x 10 ⁻³ M	Ozone	<i>Pseudomonas Putida</i> ,	Heterotrophic plate counts Degradation of primary compound and intermediates Removal of TOC	C → B	+
Suzuki et al. 1976 (17)	Polyethylene Glycol (MW 8000)	2% solution	Ozone (pH = 12) followed by Hydrogen Peroxide	<i>Pseudomonas Aeruginosa</i> PEG-K	Oxygen uptake by Warburg manometer Growth measurements	C → B	+
Suzuki et al. 1978 (15)	Polyethylene Glycol, Poly (vinyl alcohol), Poly (vinylpyrrolidone), Polyacrylamide, Sodium polyacrylate	0.4% for chemical study, 0.1% (parent compound) and 0.2% (reaction mixture) for biological study	Ozone at pH = 12	Incubation with natural bioculture	Removal of TOC, Molecular weight distribution	C → B	+ / 0

(Continued on following page)

Takahashi et al. 1994 (71)	Phenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 2,4,6-trinitrophenol, Orange II, Congo Red	1.44×10^{-3} M	Ozone	Biological Oxygen Demand	Ratio of BOD ₅ /TOC	C → B	+/-
Tanaka and Ichikawa 1989 (35)	SDS, ABS, TBC, NPE	100 mg/L	TiO ₂ /UV-light	Anaerobic digestion	Ratio of COD methane produced to initial COD	C → B	+
van der Kooij et al. 1989 (35)	Drinking Water	Not explicitly given	Ozone (0-4 mg/L)	Biofiltration	Removal of Assimilable Organic Carbon (counts of <i>Spirillum</i> and <i>Pseudomonas fluorescens</i>)	C → B	+/-
Wang et al. 1994 (77)	Bleaching Plant Effluent	1408 mg/L COD	γ-ray Irradiation	Biological Oxygen Demand	Ratio of COD/BOD ₅	C → B	+
Wang 1992 (57)	o-cresol, 2,4-dinitrophenol	200-600 mg/L 100 mg/L	Ozone, Fenton's Reagent or Permanganate	Anaerobic cultures	Biochemical Methane Potential Anaerobic Toxicity Assay	C → B	+ / 0
Wang et al. 1989 (58)	2,5-dichlorophenol	6.13×10^{-4} M 3.68×10^{-3} M	Ozone at pH 3 and 9	Anaerobic batch cultures	Biochemical Methane Potential	C → B	+ / 0
Watt et al. 1985 (2)	Effluent of Activated Sludge metabolizing mixed feed	Not explicitly given	Ozone	Mixed culture in 50-day aerobic incubation	Removal of DOC	B → C	+ / 0
Wilhelmi and Ely 1976 (76)	Acrylonitrile Waste	42000 mg/L COD	Wet Air Oxidation	Conventional industrial waste treatment	Ratio of BOD ₅ /COD Removal of COD	C → B	+
Yamazaki et al. 1983 (28)	Humic Acid (MW > 2000)	960 mg/L COD	γ-ray Irradiation	Activated Sludge	Removal percentages of COD and TOC	C → B	+
Yocum et al. 1978 (26)	Toluene Diisocyanate Waste, Polyol Waste, Styrene Waste, Ethylene Dichloride Waste	3360 mg/L TOC 830 mg/L TOC 90 mg/L TOC 400 mg/L TOC	Ozone	Acclimated seed culture	BOD ₅ and removal of TOC	C → B	+

(* See Table 2 for description of grading)

Table 2 Indicators of Effectiveness for Combined Oxidation Studies

Indicator	Effect of Combination on Overall Effectiveness
++	Dramatic increase
+	Modest increase
0	Negligible increase
-	Decrease or adverse effect

pound. The primary biological step reduces the number and concentration of compounds that may compete for the chemical oxidant, thus increasing overall removal efficiency and lowering treatment costs.

Adams *et al.* [36] examined biologically pretreated industrial wastewater containing 1,4-dioxane. This compound is recalcitrant to biodegradation but susceptible to chemical oxidation, especially by hydroxyl radical attack. Anaerobic pretreatment was used initially in some studies and resulted in the formation of metabolic by-products such as formate, acetate and propionate. Comparison between ozone/hydrogen peroxide treatment of the anaerobic effluent and a fresh dioxane solution suggested that the presence of metabolic by-products did not significantly retard dioxane degradation. This work also utilized an aerobic biological treatment following the chemical treatment, in order to further mineralize the reaction by-products. Similar results were found with 2-methyl-1,3-dioxolane [37].

Heinzle *et al.* [7] compared a variety of oxidation schemes for degrading pulp bleach plant effluents and in particular, reducing the level of adsorbable organic halogens (AOX) in these waters. Aerobic pretreatment followed by either (1) ozonation then biotreatment or (2) cyclic ozonation/biotreatment were deemed the preferable treatment options. The authors determined that a combination of treatment schemes reduced the usage of ozone for a given water quality goal. Haberl *et al.* [38] also showed that initial biological treatment of pulp bleaching effluent was preferable to initial chemical oxidation, since 50% of the original effluent was biodegradable. Subsequent chemical oxidation by ozone or ozone/gamma-irradiation led to a considerably higher overall DOC (dissolved organic carbon) and AOX elimination than did chemical pretreatment followed by biologically activated sludge treatment, due to wastage of oxidant and energy on biogenic compounds. Other combined studies of pulp and paper wastewater treatment include Berge *et al.* [39] utilizing electron beam and Sierka and Bryant [40] utilizing a combination of heterogeneous photocatalysis (with and without ozone) and ultrafiltration.

Type III. Inhibitory Compounds

Industrial waste streams often contain biodegradable compounds that possess some degree of either toxicity or activity inhibition to the bioculture. These compounds can be degraded through cometabolic activity or through the presence of specific degrader species in the microbial population. The bioculture that treats a toxic or inhibitory effluent is often less robust and more susceptible to a system upset. Chemical preoxidation has the potential to partially degrade these compounds into less toxic and more biodegradable intermediates, leading to a wastewater more amenable to biotreatment and a more robust and efficient biological process operation.

Practical use of combined treatments for Type III wastewaters presents an economic dilemma. The feed stream is

biodegradable and biological treatment is generally more cost effective than chemical treatment. The lower substrate utilization rate, high maintenance, and greater susceptibility to system upset, however, could potentially increase the biotreatment cost. Consequently, it cannot be stated in general whether a two-step chemical and biological treatment can be economically justified compared to a single step biological treatment.

Manilal *et al.* [41] degraded the inhibitory compounds methyl vinyl ketone (MVK), 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) by photocatalysis (UV-light with titanium dioxide catalyst). This chemical oxidation of MVK resulted in a decrease and eventual removal of biological inhibition as measured by the oxygen uptake activity of an activated sludge culture. Intermediate oxidation times of PCP and 2,4-DCP resulted in increased inhibition due to the early formation of more toxic intermediates, but further oxidation eventually removed the inhibitory character.

Gilbert [42] ozonated twenty-eight substituted aromatic compounds and found that continued ozonation generally led to an increase in the biodegradability of the reaction mixture, although some compounds were much more reactive than others. The authors determined that 50–70% removal of the COD was needed before the mixture was considered biodegradable. Reaction intermediates of aniline and 4-amino benzoic acid oxidation were less biodegradable than the parent compound, leading to a drop in the biodegradability of the reaction mixture. Further oxidation reestablished the trend of increasing biodegradability with increased extent of oxidation.

Type IV. Intermediate Dead-end Products

Combined processes may also be effective in the degradation of specific metabolic products, which may otherwise accumulate in the reaction medium and inhibit the microorganisms. This behavior has a higher potential of occurrence in defined biological (e.g., pure) cultures, where the enzymes necessary for total contaminant degradation, either through metabolism or cometabolism, are not present and thus a complete pathway to mineralization is not available.

Kearney *et al.* [21] found that the insecticide coumaphos was initially destroyed more effectively by the microorganism *Flavobacterium* sp. ATCC 27551 S2 than by a simultaneous combination of ultraviolet light and ozone. However, a metabolic intermediate, chlorferon, was formed which could not be degraded further. The authors used UV/ozone or ozone on this metabolic intermediate to rapidly convert it into more biodegradable fragments, which were sent in turn to a soil column for further biological metabolism.

Baxter and Sutherland [43] utilized artificial sunlight to destroy metabolic intermediates of 2,4'-dichlorobiphenyl biodegradation by a *Pseudomonas* isolate. Although the intermediates could be degraded biologically, the addition of light opened a second degradation pathway which led to more thorough destruction.

Dead-end intermediates may also be formed during chemical oxidation. Hapeman *et al.* [44] found that ozonation of atrazine led to the formation of 2-chloro-4,6-diamino-s-triazine (CAAT) which could not be degraded further. Isolation of a specialized degrader species, *Klebsiella terrigena*, was required to destroy the CAAT contaminant.

DISCUSSION

This section considers how individual process characteristics were utilized to enhance contaminant destruction, the order and relative intensity in which the oxidants were used, and the methods and parameters utilized for ascertaining the efficiency in each process.

Choice of Chemical Oxidant

The chemical oxidant used in integrated chemical-biological treatment schemes will determine the oxidation intermediates and thus both the subsequent biodegradability of the reaction products and the overall effectiveness of the system. Different intermediates may result due to the oxidizing potentials, selectivity or reaction mechanism with each oxidant. For example, many studies found increased compound destruction and eventual mineralization through advanced oxidation processes. These processes involve the *in situ* formation of hydroxyl radicals (OH•), which react quickly and non-selectively with a wide range of organic compounds [45]; such processes include UV/hydrogen peroxide, UV/ozone, hydrogen peroxide/ozone and photocatalysis [46, 47].

Conversely, molecular ozone [48] and permanganate [49], among others, react through alternative pathways and with varying oxidative strengths, which often leads to different reaction products. These pathway dependent behaviors are evident with ozonation under various pH and water conditions, because ozone can react with organics either directly, or indirectly through decomposition and formation of hydroxyl radicals (OH•) [50]. This decomposition is accelerated at high pH values or in the presence of hydrogen peroxide, UV light, or other promoters [51]. Molecular ozone will react selectively whereas hydroxyl radical is highly nonselective in its attack of organic compounds [52], thus different reaction products are often expected. The following section provides examples of how the choice of chemical oxidant affects the destruction of the primary compounds, the formation of toxic intermediates, and the biological uptake and ultimate fate of the remaining organics.

Oxidizing Ability

Lee and Carberry [53] determined that the oxidation rate of pentachlorophenol by hydrogen peroxide was negligible compared to oxidation with Fenton's Reagent (hydrogen peroxide catalyzed with ferrous ion), which produces hydroxyl radicals. Pretreatment with Fenton's Reagent also led to faster and more extensive subsequent destruction of PCP in the biological system (either activated sludge or selected microbial culture) than did pretreatment with hydrogen peroxide alone.

Somich *et al.* [24] found that UV photolysis led to rapid removal of the chlorine substituent from the herbicide alachlor. Incubation of the reaction mixture with soil microorganisms led to 60% mineralization of the compound. Ozone reaction in alachlor solution was slower than photolysis, but resulted in a more thorough destruction of the compound (through cleavage of the aromatic ring) and greater mineralization (80% at the same radiolabelled position) after incubation.

Jones *et al.* [54] found significant differences between ozone, ultraviolet light, and an advanced oxidation process (UV/ozone) during the degradation of oil shale wastewater. UV photolysis failed to significantly decrease the dissolved organic carbon concentrations or to enhance subsequent biooxidation. Ozonation mineralized 8% of the carbon and the conversion reached 26% after biooxidation. UV/ozone treatment converted nonpolar materials to more biodegradable polar compounds and provided the greatest overall efficiency, with 59% carbon mineralized after the combined treatment, rising to 87% if the bioculture was acclimated to the chemical oxidant effluent rather than the initial compound.

Kearney *et al.* [22] ozonated atrazine at pH values of 6.5, 8 and 10. Atrazine reacted slowly with ozone, but the rate increased with pH and resulted in more polar reaction intermediates. Subsequent bacterial metabolism was higher with the waste subjected to chemical oxidation at high pH values.

Potential for Toxic By-products

The chemical oxidant can also play a role in the formation of toxic by-products. Chlorine can react to form halogenated organics that may be toxic to the subsequent biological culture [55]. Bowers *et al.* [56] determined that although toxicity is generally decreased with chemical preoxidation, toxicity can increase for some compounds such as benzaldehyde, resorcinol, and salicylic acid, depending on the chemical oxidant used. Wang [57] found that potassium permanganate did not decrease the toxicity of 2,4-dinitrophenol to an anaerobic culture, although ozone and Fenton's Reagent treatment did.

Wang *et al.* [58] found that ozonation of 2,5-dichlorophenol at a pH of 3 led to increased dissolved organic carbon removal but higher toxicity values than ozonation at a pH of 9. The authors attributed the increased toxicity to an undetermined reaction product.

Effect on Fate

Oxidants can affect the fate of chemicals found in the environment. Organics that are sparingly soluble in aqueous medium will become more soluble as chemical oxidation leads to hydroxylated intermediates. Likewise, some volatile organics may also remain in aqueous solution more readily upon oxidation. Eckstein [59] found that ozone/hydrogen peroxide treatment of naphthalene and phenanthrene led to less volatile and less adsorbable reaction intermediates respectively. Thus, the organics had higher bioavailability due to pretreatment, although these particular examples did not result in higher biodegradation.

Miller *et al.* [60] found that addition of hydrogen peroxide accelerated the degrading effect of UV light considerably and led to better biological mineralization of 2,4-di- and 2,4,5-trichlorophenol. (79% and 59% mineralization of DCP and TCP respectively during a 4-day incubation after irradiation in the presence of 0.1 M H₂O₂, versus 7.7% and 5.9% after irradiation only.) UV light in the presence of hydrogen peroxide led to a greater fraction of polar intermediates and mineralization, whereas UV photolysis alone yielded reaction products exhibiting significant binding to soil. Similar results were found for the combined degradation of benzo[a]pyrene [61], although mineralization was considerably lower.

Choice of Biological Agent

The biological systems used in these combined studies are more varied than the numerous chemical oxidation processes. As with the choice of chemical oxidant, the appropri-

ate biological scheme is dependent on the characteristics of the wastewater and the goal of the treatment. Wastewater with multiple biodegradable organics may be more efficiently treated with a robust activated sludge community. Conversely, specialized bacterial species or highly acclimated cultures may be appropriate for individual, bioresistant pollutants. This section will outline and compare different microbial cultures utilized by these combined studies.

Comparison between Different Cultures

Some combined studies have used several biological systems to receive the reaction products from chemical processes [19, 60, 61]. Guillet *et al.* [13] found that radiolabelled carbon dioxide evolution rates during biodegradation of a photodegraded styrene reaction mixture were similar for a garden soil culture and activated sludge. The percentage of labelled carbon recovered was approximately 25%, however, and required addition of fresh sludge cultures to attain appreciable mineralization (> 70%).

Other studies considered addition of specific degrader species to a bioculture in order to accelerate biodegradation of specific compounds [25]. Kearney *et al.* [22] added a *Pseudomonas* strain to soil microorganisms; soil amended with the *Pseudomonad* increased mineralization of formulated atrazine rapidly and attained higher $^{14}\text{CO}_2$ recovery ($\approx 60\%$) than did unamended soil columns ($\approx 40\%$).

Lee and Carberry [53] compared activated sludge to a selected microbial consortium, developed specifically to degrade PCP. Biodegradation of untreated PCP was slow for both cultures. Once the PCP was chemically pretreated, however, the microbial consortium degraded PCP and produced chloride ion more effectively than did the activated sludge culture. This result will not hold for all compounds and treatment systems, as described below.

Comparison between Acclimated and Nonacclimated Cultures

An interesting aspect of the biological processes used in combined treatment is the effect of acclimation on the degradation ability. Acclimation of microorganisms to the substrate of interest is widely used to maximize the removal efficiency of specific compounds which are difficult to biodegrade. This is accomplished by increasing the feed concentration of the compound of interest over a period of time to allow for the growth of microorganisms which can utilize the compound as a carbon or nutrient source. In a combined chemical and biological treatment, however, the substrate degraded by the bioculture may not be the original compound to which it was acclimated, but one or more reaction intermediates. Degradation of these intermediates will depend on whether the specific microorganisms or others present in the microbial community have the necessary enzymes (chemical oxidation intermediates may or may not be the same as metabolic intermediates) and ability to successfully biodegrade them. In some cases, the acclimated cultures may have an advantage in degrading the intermediates due to their specialized metabolic pathways. Likewise, a culture not stringently acclimated may have a larger number of species which are more adaptable in degrading the intermediate. Thus, a question arises concerning the usefulness of strongly acclimating mixed cultures versus utilizing more robust unacclimated cultures in these situations. Also, if acclimation is used, should the culture be acclimated to the original compound or to one or more of the primary intermediates?

Using reaction products arising from Fenton's Reagent pretreatment of phenolic waste, Bowers [62] compared the biodegradation by acclimated and unacclimated activated sludge cultures. The acclimated culture was initially more

effective at degrading wastewaters, especially when the water contained only 2,4-dichlorophenol and not a mixed industrial waste. As the chemical reaction time was extended, however, the substrate uptake by the unacclimated culture (measured in terms of TOC and COD) increased and in some instances exceeded that of the acclimated culture. This result suggests that acclimation of a more diverse culture to reaction intermediates may be more efficient than acclimation to the original waste stream.

Hu and Yu [63] also found that unacclimated cultures generally biodegraded ozonation by-products of chlorophenols better than untreated chlorophenols. The authors attributed this to either the destruction of the parent compound or the formation of more biodegradable intermediates. Pretreatment had an adverse effect, however, on some of the biological cultures that were acclimated to the parent compounds: reduction of COD by acclimated cultures was better for some of the untreated samples than for samples ozonated for a short time (6 to 10 minutes).

Jones [54] determined that the combination of UV/ozone followed by biological treatment with a culture acclimated to wastewater from an oil shale process led to an overall destruction of 59% DOC. A culture directly acclimated to the UV/ozone reaction products, however, provided 87% overall reduction in DOC. Stable microbial cultures could not be developed for reaction products from either ozone or UV light pretreatment.

Eckstein [59] found that after thirty minutes of ozone/hydrogen peroxide treatment, the reaction products of pentachlorophenol oxidation were mineralized to the same extent by a generic mixed culture as a culture composed of specific degraders of PCP.

Pure Cultures

Pure microbial cultures have been cultivated and genetically engineered to degrade chemical compounds that are generally resistant to biodegradation by conventional treatment. This approach can be effective for highly defined wastes or wastes which are highly toxic to other microorganisms. Treatment with pure cultures may be effective only if the objective is to reduce the concentration of the target compound. Complete mineralization may not be achieved, resulting in the accumulation of end products and requiring either the addition of a second process (as seen with Type IV wastewater) or a more robust microbial community.

Anaerobic Cultures

Anaerobic treatment has also been used in combined studies, both after [16, 57, 58, 64] and before [36] chemical treatment. As found with some Type II wastewaters, anaerobic pretreatment can be effective at degrading compounds while producing a reduced reaction by-products load.

Practical Aspects of Combining Processes

Combining chemical and biological processes poses interesting challenges in conducting research and operating a full-scale plant efficiently. It may be important that the chemical oxidant and bioculture do not mix. Ozone, for example, is used as a disinfectant and would be detrimental to the biological culture if toxic residual amounts remained from pretreatment. High concentrations of hydrogen peroxide can also prove detrimental to the bioculture although relatively low concentrations do not pose a serious problem for microorganisms. Carberry and Benzing [65] found that increasing the hydrogen peroxide concentration relative to TCE or

PCP increased biodegradability up to a point, but at an initial molar ratio of 6:1 (H_2O_2 :pollutant) ($4.7 \times 10^{-4} - 3.3 \times 10^{-3}$ M), the high residual levels of peroxide adversely affected the bioculture. Barton and Drake [66] found increased toxicity in samples of blow heat condensates, which were pretreated with high levels of hydrogen peroxide (8.8×10^{-2} M), despite taking steps to quench the residual peroxide (2.9×10^{-2} M). Heinzle *et al.* [7] experienced a pump failure that led to a high ozone level in the biological system, and subsequent deactivation of the bioculture. Kearney *et al.* [21] made positive use of the cell-killing abilities of chemical oxidation. UV/ozone, applied after biological oxidation by a specialized bacterial species, not only destroyed chemical intermediates but also killed the organism and prevented its viable release into the environment.

Special steps were taken by some researchers to prevent the introduction of chemical oxidants into subsequent biological processes. These included holding the chemical reaction mixture for a day to dissipate residual ozone [54, 67], adding catalase [56, 62, 66] or sodium sulfite [36] to solutions with residual hydrogen peroxide or adding sodium sulfate to reduce the potassium permanganate residual [56].

The chemical reaction conditions also require steps to prepare the reaction mixture for biodegradation. The use of Fenton's Reagent is most effective at low pH values (3–5) [68], thus adjustment to higher pH levels may be necessary prior to biodegradation [53, 65]. Removal of iron hydroxide precipitate may also be required after using Fenton's Reagent, however Gilbert [69] noted that an activated sludge unit worked well despite the presence of such a precipitate. Potassium permanganate forms a MnO_2 precipitate that must be removed [56, 57], and photocatalysis requires removal of the metal oxide catalyst [16, 41] before subsequent biodegradation.

Effect of Reaction Time

Decreased Efficiency

The reaction time in the chemical oxidation process is important in a combined process. Longer oxidation times lead to a greater degree of oxidation and higher removal when chemical oxidation is the sole treatment. Higher overall removal does not necessarily occur at the long chemical oxidation times in a combined system, however. When a biological process is receiving the chemically pretreated effluent, excessive chemical oxidation may result in highly oxidized products possessing little metabolic value for the microorganisms. Large oxidant doses could be wasted on easily biodegradable reaction intermediates resulting in decreased system efficiency.

Stowell *et al.* [70] studied the degradation of 2-chlorophenol by ozone. Two major reaction intermediates, chlorosuccinic acid and oxalic acid, appeared sequentially during ozonation. The average growth rate studies using *Pseudomonas Putida* on the solutions of the individual intermediates indicated that the greatest biological degradation occurred with the chlorosuccinic acid intermediate, while the oxalic acid was not utilized.

Adams *et al.* [36] found that the key to an effective process was complete removal of the parent compound, 1,4-dioxane. The point of disappearance of this compound corresponded to the highest BOD level of the effluent during chemical oxidation. Further chemical oxidation only served to decrease the residual biological oxygen demand.

Gilbert [69] determined that partial oxidation of aromatic and EDTA-containing industrial wastewater with Fenton's Reagent led to a highly biodegradable effluent, but further oxidation led to lower BOD₂₀:COD ratios. This latter result suggests wastage of the chemical oxidant on biodegradable

compounds. This phenomenon was also found during ozonation of conventional biological treatment effluent [67] and UV/ozone treatment of oil shale wastewater [54]. Takahashi *et al.* [71] also found an optimum oxidation time for ozonation of nitrophenols and two synthetic dyes (Congo Red and Orange II). Ozonation led to more biodegradable mixtures but further oxidation after a dose of 2.3–3.8 mg ozone/mg TOC nitrophenols or 1.3–1.7 mg ozone/mg TOC synthetic dyes led to a decrease in the BOD₅:TOC ratio of the reaction mixtures. Speitel *et al.* [72] found that ozonation of one lake water at high ozone concentrations (5 mg O₃/mg TOC) led to destruction of trihalomethane precursors, but this dose was not preferable since the oxidant was wasted on biodegradable organics. Significant amounts of bromide were also oxidized to bromate at the higher ozone concentrations.

Janssens *et al.* [34] found that small ozone doses (2 mg/L) increase biological activity in downstream activated carbon filters, and thus extend the filter lifetime and removal efficiency. Increased ozonation did not significantly enhance this positive effect but did cause higher production levels of assimilable organic carbon (AOC). This increased AOC load was less adsorbable on the carbon and resulted in a faster breakthrough of the filter, although TOC removal was higher at the high ozone concentrations.

Formation of Toxic By-products

Short chemical oxidation times may prove detrimental due to the formation of toxic intermediates. Manilal *et al.* [41] found that an intermediate product of the photocatalytic oxidation of PCP and 2,4-dichlorophenol led to inhibition of an activated sludge culture. This effect was removed, however, with further chemical oxidation. Bowers [62] found slightly higher toxicity values for 2,4-dichlorophenol solutions after partial oxidation, and subsequently decreased toxicity as the oxidation time was extended. This behavior has also been reported with wet air oxidation of 2-chlorophenol [1] or trinitrotoluene wastewaters [73], and ozonation of aniline [5, 42] or amino-substituted phenols [74].

Measure of Biodegradability

Gross Parameters

Methods for reporting biodegradability in these systems vary considerably. Gross estimators of water quality include biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and dissolved organic carbon (DOC). A measure of oxidation state of the wastewater can be estimated from the formula [75],

$$\text{Average Oxidation State} = \frac{4(\text{TOC} - \text{COD})}{\text{TOC}} \quad (1)$$

where TOC is in mg Carbon/liter and COD is mg Oxygen/liter. Other common methods report the ratio of either BOC/COD [42, 69, 76, 77] or BOD/TOC [14, 71, 78]. These parameters may be used to compare the biodegradability of the wastewater as a function of chemical oxidation time. Yamazaki *et al.* [28] noted, however, that an increasing ratio with oxidation time may not necessarily indicate increasing biodegradability but only a reduction in the TOC or COD. Reductions in BOD, COD and TOC are also used to report the destruction of organics during chemical and biological oxidation. These measures, however, give little insight into the biological system mechanisms.

Other biodegradability measures include substrate destruction, oxygen uptake, EC₂₀ toxicity measurements, cell growth counts, intracellular ATP levels and evolution of carbon-14

labelled CO₂. Eckenfelder [79] suggested utilizing a fed batch reactor to measure oxygen uptake and to assess biodegradability and toxicity of wastewaters.

Kinetic Measurements

A few studies have reported biodegradability in a kinetic rate form. This information is more quantitative than the previous measures and can be used in the design of biological reactors and prediction of process performance. These studies characteristically report substrate removal rate as following Monod kinetics,

$$\frac{dS}{dt} = \frac{q_{\max} S}{K_s + S} X \quad (2)$$

where q_{\max} is the maximum specific substrate removal rate, K_s the half velocity constant, S the substrate concentration and X the biomass concentration. Lee and Carberry [53] measured the specific substrate uptake rate, $SUR = (dS/dt)(1/X)$, and used a curve fitting program to determine the q_{\max} and K_s values. Carberry and Benzeng [65] also used this method in terms of COD for the removal of TCE, PCP and toluene. Both studies utilized electrolytic respirometry to obtain oxygen uptake data.

Bowers *et al.* [62] determined instantaneous q_{\max} values from fed-batch data by measuring

$$q_{\max} = \frac{(S_{in} - S_r)}{X} \quad (3)$$

where S_{in} = substrate input rate and S_r = substrate response within the fed-batch reactor. These values of biodegradability were used to compare the results from different chemical oxidation times and biological cultures.

Stover *et al.* [80] measured the specific substrate uptake rate during the degradation of acrylonitrile, 2,4-dinitrophenol or 1,2-dichloropropane and their ozonation products. Narkis and Schneider-Rotel [67] reported first order biodegradation rate constants for the destruction of TOC and COD in municipal and industrial wastewater treatment effluent.

Measurement of Efficiency in Process

Goal for Efficiency

The measure of effectiveness depends on the treatment goal. The degree of mineralization of all organics may be the measure of effectiveness if high purity water or specified TOC effluent limits need to be attained. Other treatments may consider the primary goal as total reduction of toxicity or the specific removal of the primary compound. Determining a goal is an essential step in combined studies because it helps to define process efficiencies and provides a basis for comparison and eventually optimization within the process.

Comparisons between Individual Efficiencies

The global efficiency for the combined processes considered in this paper consists of a chemical and a biological component. How these individual process efficiencies are computed and compared is important, because these values may be the basis of discovering optimal reaction conditions for the integrated system. As seen in this review, the initial process step strongly influences the effectiveness of the second process and hence the global efficiency. Simply comparing the percentage of the treatment goal attained in each

step may not be adequate in all cases. For example, 95% of a reaction mixture may be mineralized in the second biological process whereas without pretreatment, mineralization may be negligible. Chemical pretreatment plays a large role in achieving the high global mineralization value although substantial mineralization did not occur in that step. A scenario such as this demonstrates the need for measuring the individual efficiencies while requiring attainment of the overall treatment goal.

The simplest method compares the effectiveness of each successive process by computing a ratio of the percentage of the treatment goal attained in a single process to the total potential efficiency.

$$X = \frac{\% \text{ of Treatment Goal Attained in Chemical Step}}{100\% \text{ Attainment of Treatment Goal}} \quad (4)$$

$$Y = \frac{\% \text{ of Treatment Goal Attained in Biological Step}}{100\% \text{ Attainment of Treatment Goal}} \quad (5)$$

$$Z = X + Y \quad (6)$$

where Z is the total efficiency of the combined process. The major criterion is that the desired Z value is attained. Further analysis can then be done concerning the amount of treatment accomplished in the respective processes, i.e., ratios of X/Z and Y/Z . Variables, such as process time or oxidant strength, can be changed to measure their impact on these ratios.

Yamazaki *et al.* [28] performed this type of analysis in the treatment of humic acid solutions by a combination of gamma-irradiation and activated sludge. Efficiencies in terms of COD and TOC reduction were calculated for each oxidation step and at different time intervals during the biological oxidation. The authors compared the relative efficiencies of the chemical and biological treatments by determining ratios of X/Z and Y/Z . High Y/Z ratios were considered optimal (assuming that high Z values could also be attained) because these imply that a large amount of COD and TOC destruction occurred in the biological system, which the authors considered economically favorable. Intermediate oxidation doses led to the preferred efficiency ratios, although the BOD/COD and BOD/TOC ratios continued to increase with increased chemical oxidation. Higher chemical doses tended to reduce the positive effect on the biological culture found with intermediate doses.

A second method considers the ratio of efficiency of the combined process to the efficiency that would be accomplished if either of the individual processes were used solely, (assuming equal reaction time, oxidant dose, economic cost, or other factor deemed important.) This ratio provides a measure of the synergism obtained when combining processes and allows for comparison of this measure as a function of system variables such that optimal reaction conditions may be identified. Many studies listed in Table 1 have reported their results in comparison to those attained by utilizing one of the individual processes, although rarely both. The synergism found with respect to each individual process may be extremely valuable, especially when Type II or III wastewaters are degraded, since theoretically, either the chemical or biological process could be used for complete mineralization of the waste.

Constraints on System

Measures of efficiency will only be important within the constraints imposed on the particular treatment system. These constraints may appear as economic and physical limitations that are traits of the particular waste treatment facility, such as reactor volumes, volumetric flow rate or treatment time. With no limitations, the most effective treatment would simply allow an indefinite reaction time until the treatment goals

are satisfied. Only in the presence of limitations can an efficiency be defined and compared under different reaction times and conditions. The particular limitations that restrict a treatment plant's operation may also create and shift regions of optimal operation due to the synergy within the integrated system.

Esplugas and Ollis [81] constrained a hypothetical two-stage process using chemical oxidation followed by biological treatment. Degradation of a recalcitrant compound and its assumed sole intermediate followed first-order degradation rates in the chemical process while the intermediate followed Monod kinetics (equation 2) in the biological system. The constraint of a fixed overall reactor time was set and the individual residence times were varied to determine the effect on substrate degradation and system efficiency. In this study, the respective efficiencies of the chemical and biological system were,

$$\eta_C = \frac{S_{AO} - (S_{AC} + S_{SC})}{S_{AO}} \quad (7)$$

$$\eta_B = \frac{S_{SC} - S_{SB}}{S_{AO}} \quad (8)$$

where S_{AO} is the concentration of recalcitrant compound A entering the chemical reactor (mg/L), S_{SC} is the concentration of intermediate compound(s) S leaving the chemical reactor (mg/L), S_{SB} is the concentration of intermediate compound(s) S leaving the biological reactor (mg/L) and S_{AC} is the concentration of compound A remaining after chemical oxidation. The overall system efficiency was the sum of chemical and biological efficiencies,

$$\eta_G = \frac{S_{AO} - S_{SB} - S_{AC}}{S_{AO}} \quad (9)$$

The authors found that a maximum efficiency was present and that efficiency goals could be achieved under a variety of reaction times (see Figure 1). More importantly, the chemical and biological processes accomplished different percentages of the total degradation at these different conditions. Given treatment goals could be attained under a variety of operating conditions and oxidant usage, and an economic optimum could be sought while holding the treatment objective constant. For the example in Figure 1, an 83% efficiency can be achieved by 7.2 hours in a (photo) chemical reactor alone, or by 3 hours in the (photo) chemical reactor and 7 hours in a biological reactor. If the total fixed and operating costs of the bioreactor are less than about 4/7 of the chemical reactor (on a volume basis), as is often the case, then the combined system would be less expensive. Changes in relative reactivity of the primary contaminant and intermediate in both the chemical reactor and bioreactor or in reactor operation and

type will affect these results substantially. A model analysis of chemical oxidation followed by an activated sludge process or fixed column bioreactor considers these additional cases [82].

RECOMMENDATIONS FOR FUTURE STUDIES

Recent studies are reporting in greater detail information that better elucidates the positive effect found by applying chemical and biological processes in series. Identification of intermediates and determination of their toxic or inhibitory properties and their susceptibility to further chemical or biological degradation is important in expanding this understanding. There is a great need, however, for a more rigorous approach to reporting efficiencies and modeling the overall degradation. Such information could assist in the design and determination of optimal operating conditions of integrated processes. Below are some suggestions for future studies.

Biological Studies Beyond Biodegradability

Numerous studies have reported improvement in biodegradability, after chemical oxidation or physical process treatment, by measuring biological oxygen demand or assessing toxicity by measuring an EC_{50} value. These gross parameters provide little information about the conversion pathways and ultimate fate of a parent compound, its reaction intermediates and the final effluent quality in the bioreactor.

To better study the effects of one process on the other and to predict behavior in actual process streams, biological studies that receive pretreated waste need to be run in systems which mimic an actual process. Information concerning the rate of substrate degradation, extent of mineralization and ultimate fate of all compounds can be determined from these systems. The extent of conditioning of the microbial culture to the parent compound, reaction intermediates, or synthetic mixtures also needs to be reported. As cited above, acclimation of the biomass to a particular substrate may accelerate its biodegradation but hinder the biodegradation of other substrates.

Intermediates and their Properties

The reaction intermediates formed in combined processes are often the key to the efficiency of the system. If chemical oxidation is followed by biological treatment, the resistance to further chemical oxidation, the biodegradability and the toxicity of these intermediates all directly influence the effectiveness of each treatment step and determine when it would be optimal to switch processes. Future studies should recognize this element and report the individual intermediates formed. A better rationalization of the kinetic phenomena that occur and of process synergy can be gained through such information.

Kinetic Models (both chemical and biological)

None of the studies listed in Table 1 presented an overall kinetic model for the combined process. Such a model would be required for the design of combined processes and the determination of optimal operating regions in terms of efficiency or economic cost. The effect of changing such system variables as flow rates, reactor volumes, organic load etc. on the total efficiency of the system is important and could conveniently be predicted with an overall engineering model. The work by Esplugas and Ollis [81] and Scott and Ollis [82] is a step in this direction.

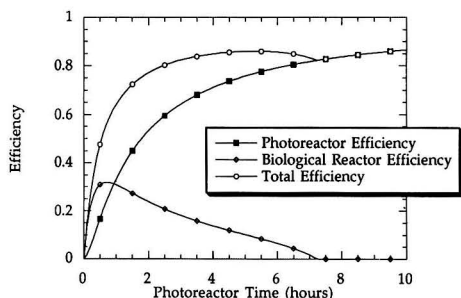


FIGURE 1. Efficiency as function of photoreactor residence time (Esplugas and Ollis [81]).

Biological Kinetics with Multiple Substrates and/or Inhibition

The few kinetic models to date often ignore the kinetic competition that occurs in both processes as multiple reaction intermediates are formed. For example, in the chemical reactor, competition for the oxidant will occur in systems that contain a mixture of the parent compound and primary intermediates. Oxidant competition may also occur when biotreatment is followed by chemical oxidation [36], as the recalcitrant target compound competes with metabolic by-products or with biogenic materials that were not completely removed.

Effluents from chemical pretreatment processes will include multiple solutes with different biodegradabilities. Studies to date which have adopted biological kinetic models have not considered multiple substrates. Also, models have not been extended to circumstances where a fraction of the compounds present may inhibit biodegradation at high concentrations. This is an important kinetic case (Type III wastewater) because application of combined processes is potentially beneficial for this type of wastewater.

Comparisons of Relative Efficiency in Each Process Step

The final recommendation for combined studies is to analyze and present data in terms of global and individual process efficiencies. Determination of efficiencies indicates the attainment of a specified treatment goal, provides a measure of the synergistic effect achieved, if any, as a function of system variables, and affords information concerning the relative work done by each process toward attainment of the treatment goal.

CONCLUSIONS

Combination of chemical and biological processes leads to greater and more thorough destruction of many organic contaminants in wastewaters. The biodegradability or recalcitrant character of the wastewater often suggests the particular processes and order of treatment to be used. Four types of wastewater have been identified in which a two-step combination of processes should show potential for significant improvement over single step processes.

Pretreatment usually enhances the second process. Initial chemical oxidation can destroy compounds that would otherwise limit the effectiveness of the biological unit, and may produce intermediates which are amenable to further degradation. Examples finding adverse effects due to pretreatment have also been identified. These effects may be due to the formation of toxic by-products or recalcitrant compounds, or chemical removal of compounds for which biological removal is more efficient.

Similarly, the biological system, when utilized as a pretreatment, can favorably affect the subsequent chemical oxidation by removing biogenic compounds that would otherwise compete for the expensive chemical oxidant. Specific microbial degraders could be employed to selectively remove problematic compounds.

The properties of the primary reaction intermediates play a key role in the efficiency of the total process and provide insight into the synergism observed within the process coupling. This synergy will be lost, however if the pretreatment is too short to effect significant change on the wastewater or so long that the processes are decoupled. Therefore, a maximum overall effectiveness is expected to lie at some intermediate operating condition which is dependent on the physical, chemical and biological properties of the reaction intermedi-

ates and any economic or physical limitation imposed on the system.

Only a few studies have utilized kinetic models to represent substrate degradation, with a majority of the biological studies relying on gross parameters. More work needs to be done on kinetic and reactor modeling of both processes with respect to the intermediate species. Competition for chemical oxidant by the compounds and multiple substrate kinetics for biological mixed cultures are two examples for further study.

The global efficiency of the combined process is a key performance measure of these systems. The treatment objective can indicate what data is to be measured and the manner in which efficiencies are computed and compared. More work needs to be done on how characteristics of the system enhance or limit the individual and global efficiencies and eventually the overall treatment cost.

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Physical Conditioning to Enhance Bioremediation of Excavated Hydrocarbon Contaminated Soil at McClellan Air Force Base

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McClellan Air Force Base conducted an evaluation of an aerated-pile composting process and a slurry bioreactor process for biologically treating excavated hydrocarbon-contaminated soils while controlling emissions of volatile organic compounds. A large aspect of process evaluation was development of soil conditioning steps prior to biological treatment. The conditioning steps evaluated were: soil washing, using trommel and attrition scrubbers; and milling, using rod and hammer mills. Scrubbing was not effective at producing a consistently clean oversize fraction. Milling was effective at reducing the size of larger material and breaking agglomerates. Bioremediation results indicated both processes capable of greater than 90 percent reduction in hydrocarbon levels within 90 days.

Aerated-pile composting was the preferred process because it required less operation and maintenance and more easily handled varying soil characteristics. A full-scale treatment process was developed and is described.

INTRODUCTION

Ex situ biological soil treatment processes typically require soil handling and conditioning steps. The soil must be excavated, transported, conditioned, and placed into the treatment process. The effort required for conditioning will depend on the requirements of the treatment process, the type of contaminant, and the physical characteristics of the soil such as mineral type, particle size, particle structure, and water and organic content. The success of the biological process may depend on the success of the conditioning process to provide conditions amenable to biodegradation [1-2]. The variability of a soil's physical characteristics must be considered when designing a conditioning process. If site soils vary appreciably, then additional or more robust processes will be required than those for soil with little variability.

The United States Air Force is undertaking cleanup of hydrocarbon-contaminated soils at McClellan Air Force Base (McClellan AFB) in Sacramento, California. Part of this work was the evaluation of two bioremediation processes for treatment of excavated hydrocarbon-contaminated soils. The two processes evaluated were aerated-pile composting (APC) and slurry bioreactor treatment combined with prepared-bed land treatment (SB/LT). These processes were evaluated because they offered the means to control the release of volatile organic compounds (VOCs) during treatment. McClellan AFB has permitted limits of the amount of total VOCs that can be released.

Aerated-pile composting is a bioremediation technique in which soil is piled on a prepared pad, air is pulled (or forced) through the pile to aerate the soil, and water and nutrients (if needed) are added to maintain conditions conducive to mi-

crobial metabolism [3]. The slurry bioreactor and land treatment process is a bioremediation technique which combines slurry treatment and land treatment [4-5]. Slurried soil is mechanically mixed in an aerated reactor for a period only long enough to initiate biological degradation and to remove (biodegrade or strip) VOCs. The slurry is then dewatered and placed in a prepared bed for additional treatment using land treatment techniques where the soil is periodically aerated by tilling and watered to prevent drying.

Conditioning steps prior to either the APC or the SB/LT techniques are important to achieve consistent results. If the soil in the APC piles is not homogeneous in terms of particle size and distribution within the pile, oxygen and moisture levels may vary throughout the pile because of differing permeabilities. Also, if "clumps" or "clods" of clay agglomerates are present, little treatment will occur inside of them because the tight soil structures restrict contact between contaminants contained within and microorganisms, oxygen, water, and nutrients. Because the SB/LT technique requires that soil be processed to a particle size and solids distribution that can be suspended in the reactor, clay agglomerates and cemented duripan must be broken and sized prior to addition to the reactor, or they will settle to the bottom and interfere with mixing.

The purpose of this paper is to describe the development of the soil conditioning steps that were selected to augment biological treatment. The selected conditioning steps were combined with the APC process to form a recommended design for a full-scale excavated soil treatment facility.

SOIL CHARACTERISTICS AT McCLELLAN AFB

McClellan AFB is underlain by a thick (> 300-meter) section of unconsolidated sediments deposited by streams draining the Sierra Nevada. The uppermost deposits are termed the Riverbank Formation which is approximately 15 to 30 meters thick at McClellan AFB. The Riverbank Formation is composed of a heterogeneous assemblage of fluvial deposits laid down by shifting streams that drained the Sierra Nevada in Pleistocene time. These streams left channel-like structures of sand, gravel, silt, and clay which provide little correlation of materials over short distances.

Most of the soils have been in place long enough to have developed a silica cementation (duripan) that averages 0.5 to 1 meter in depth, although it may extend to several meters in certain locations. Surface textures are dominantly loam and sandy loam, underlain by finer-textured loam and sandy clay loam horizons over duripan. Soil infiltration rates range from 1.5 to 5 centimeters per hour, depending on local amounts of clay and duripan. The local soils are generally classified as San Joaquin fine sandy loam, Fiddymint fine sandy loam, or San Joaquin-Zeralfc Arents complex. However, in many areas of McClellan AFB, natural soil conditions are no longer represented because of excavation and construction activities.

TEST SOILS

Soils from two areas of McClellan AFB were used for testing. One soil was from the east side of the Base and had been excavated during construction of a parking lot (PL). The other soil was from the west side of the Base and was excavated from an area near Building 720 (B720). The two soils used for testing were fine-textured and can be classified as either silty sand or clayey sand with varying amounts of gravel, according to the Unified Soil Classification System.

The PL site was a fuel and oil disposal area adjacent to a troop issue area. Previous sampling results indicated variable total petroleum hydrocarbon (TPH) contamination with con-

centrations as high as 43,200 mg/kg on a dry weight basis (EPA Method 418.1). The B720 site was also a fuel and oil disposal area. Previous sampling results indicated variable TPH contamination, with concentrations ranging from 1,200 to 5,400 mg/kg dry basis (EPA Method 418.1).

The extreme soil variability over short distances that can exist at McClellan AFB can be illustrated by observations made during excavation of the B720 soil. It was noted by visual observation that the first 0.5 meters below ground surface (bgs) appeared to be clean gravel/sand foreign fill and that the zone from 0.5 to 1.1 meters bgs was sands and silts with grey staining. The 1.1- to 1.3-meter zone was a duripan that was fine-grained and cemented and appeared heavily contaminated. The zone from 1.3 to 1.9 meters bgs appeared to be sands and silts and was stained grey. The zone from 1.9 to 2.1 meters bgs (bottom of hole) appeared to be red sands.

When the B720 soil was excavated, the duripan layer was broken up and transformed into "clods" or "clumps" These clods were also present in the PL soil. The clods ranged in size from less than 2 centimeters to up to 30 centimeters. In both soils, the clods were permeated thoroughly by the contamination and were tough and difficult to crush manually. The proportion of the soil that was clods varied between B720 and the PL soils. On the basis of the relative thickness of the duripan layer in the B720 soil strata, the duripan represented approximately 10 percent of the excavated contaminated soil. For the PL soil, measurements indicated that approximately 20 percent of the soil was greater than 2-centimeters, and that most of this material was duripan clods.

EVALUATION OF POTENTIAL CONDITIONING PROCESSES

Evaluation of potential conditioning processes involved three steps: initial soil characterization, bench-scale testing, and pilot-scale testing. The procedures and results of each step are described below.

Initial Soil Characterization

Both soils were initially characterized by wet-screening to determine the contaminant distribution as a function of soil particle size ranges. The screening was performed one screen at a time using a mechanical agitator. One-quarter-inch, 20-mesh, 48-mesh, and 100-mesh screens were used. Soil and water samples were collected and analyzed for TPH (EPA Method 8015 Modified).

The two test soils varied dramatically by type of contaminants, size distribution, and contaminant concentration in various size distributions, as shown by the results summarized in Table 1. In addition, the B720 soil varied significantly in terms of particle size and contamination level over very short distances. For instance, the 0.5- to 1.1-meter-deep layer had 3 percent of the soil greater than 1/4-inch in size with a TPH level of 61 mg/kg; the 1.3- to 1.9-meter-deep layer had 26 percent of the soil greater than 1/4-inch with a TPH level of 697 mg/kg; and the 1.9- to 2.1-meter-deep layer had 9 percent greater than 1/4-inch with a TPH level of 294 mg/kg. This diversity is likely due to varying amounts of agglomerated soils as well as differing quantities of clay and silt within the different layers.

Mineralogical examinations were also conducted on both soils. The B720 soil sample was predominantly quartz and feldspar of sand-size range, with abundant agglomerates of silt-sized quartz and feldspar cemented by clay minerals, and possibly some chalcedonic quartz or opaline quartz. These agglomerates showed varying degrees of competence; some could be easily crushed and dispersed in water, but others could not. The PL soil sample was predominantly fine, sand-

Table 1 Bench-Scale Wet Screening Characterization Results

Soil	1/4-inch screen (6.5 mm)		20-mesh screen (0.85 mm)		48-mesh screen (0.30 mm)		100-mesh screen (0.15 mm)		Bottom Pan		Sieve Water	
	Percent of Soil Retained ^a (%)	TPH ^b (mg/kg)	Percent of Soil Retained	TPH	Percent of Soil Retained	TPH	Percent of Soil Retained	TPH	Percent of Soil Retained	TPH	Volume (liter)	TPH (mg/l)
Parking Lot	16.7	1,680	18.1	2,850	NA ^c	NA ^c	29.7	1,290	35.5	2,250	11.5	967
Building 720 0.5- to 1.1- meter-deep layer	3.0	61	1.1	84	18.3	123	22.7	721	54.9	3,450	37.0	5,030
Building 720 1.3- to 1.9- meter-deep layer	26.4	697	9.9	594	NA ^c	NA ^c	28.1	176	35.6	957	26.0	152
Building 720 1.9- to 2.1- meter-deep layer	9.3	294	19.7	36	NA ^c	NA ^c	58.1	31	13.0	492	24.0	147

^aPercent retained by dry weight basis.

^bTPH by EPA Method 8015 Modified (dry weight basis).

^cNot applicable because this screen size was not used.

sized quartz and feldspar, and also contained abundant agglomerates of silt-sized quartz and feldspar, plus fine-grained mica and clay minerals. The sample also contained minor quantities of coarse, liberated mica flakes.

Bench-Scale Testing

Bench-scale testing consisted of simulating three types of process equipment that potentially could be key components in the soil conditioning steps for the SB/LT process. Trommel scrubbing, attrition scrubbing, and rod milling operations were tested. Trommel and attrition scrubbing were evaluated as potential methods to scrub and segregate the coarser-sized from the finer-sized fractions. The rod mill was evaluated as a means to mill the oversized soil fraction to a size that could be maintained in suspension in the slurry bioreactor.

A trommel scrubbing device consists of a rotating horizontal drum with interior baffles. As rotation occurs, the soil particles are reduced and separated, exposing more surface area to the washing fluid. To simulate trommel scrubbing, a 5,000-gram soil sample and 5,000 grams of tap water were placed into a 20-liter, high-density polyethylene bottle which was placed in a horizontal position and rotated at 35 revolutions per minute. Both the PL and B720 soils were bottle-rolled using residence times of 5, 10, and 20 minutes.

Similar to the trommel scrubber, the rod mill consists of a rotating horizontal drum. However, within this horizontal drum are many steel rods that increase the amount of mechanical energy available for particle size reduction and to break apart consolidated clays. A soil sample was placed in a laboratory rod mill measuring 18 centimeters in diameter and 23 centimeters long. Four rods of various diameters weighing a total of 2.16 kg were used. The mill was rotated at about 43 revolutions per minute for 5 minutes. Tests were conducted on each soil at 50 percent solids by weight and using 40°C water and surfactant (Polystep A7).

The attrition scrubber consists of a series of blades which vigorously propel the soil into collisions with itself, thereby causing a size reduction and separation of the soil particles. Attrition scrubbing is a more intensive scrubbing method than

trommel scrubbing for finer-sized soil fractions. The attrition scrubbing tests were conducted using a 1-liter Wemco laboratory mill. A soil sample was scrubbed with the trommel scrubber at a 20-minute retention time and screened at 20 mesh. The material that was less than 20 mesh was used for the attrition scrubbing tests. Tests on PL and B720 soil were performed at 45 and 80 percent solids by weight, and at retention times of 15 and 30 minutes at each percent solids. Following attrition scrubbing, the material was wet screened on a 100-mesh screen.

The overall conclusion from these tests was that for both soils trommel and attrition scrubbing did not adequately wash particles larger than 20 mesh. TPH contamination in excess of 100 mg/kg was still present. This was attributed to the cemented structure of the soil particles. Trommel and attrition scrubbing were not capable of supplying sufficient energy to break the cementation and to liberate the contamination. Rod milling was capable of breaking the cementation of the B720 soil and reducing the TPH contamination in the soil greater than 100 mesh to less than 100 mg/kg. However, rod milling was not capable of breaking the cementation of the PL soil. TPH contamination in excess of 100 mg/kg remained on the PL soil size fraction greater than 100 mesh.

Pilot-Scale Testing

Pilot-scale testing of the SB/LT process and the APC process was commenced following the bench-scale testing. Testing of the SB/LT process was conducted at the facilities of Hazen Research, Inc. (Hazen), in Golden, Colorado. The APC process pilot-testing was performed at McClellan AFB.

Slurry Bioreactor/Land Treatment Testing

Testing of the PL and B720 soils was conducted separately. A similar pilot-scale system was used for each soil. A process schematic is presented in Figure 1.

The test soils were shipped to Hazen for testing. The B720 soil had much lower concentrations of contaminants than

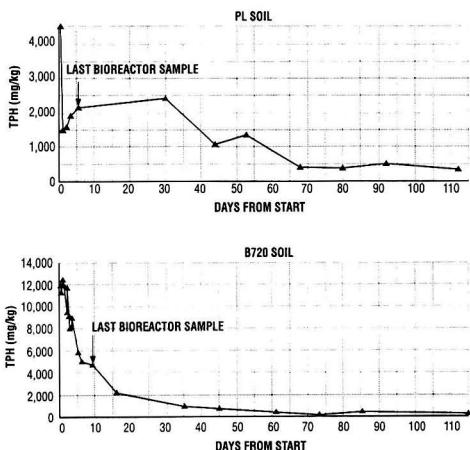
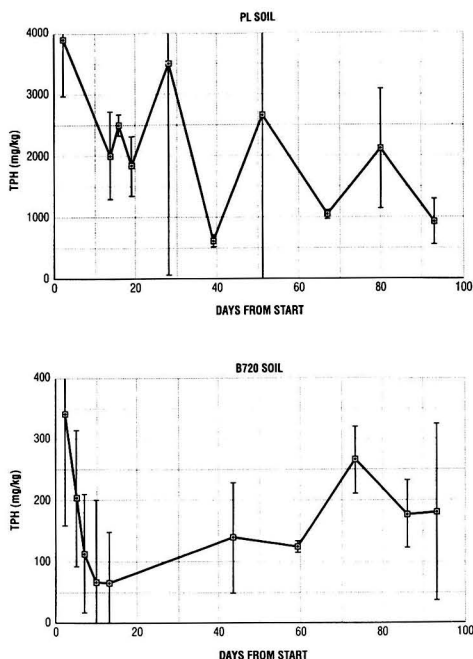


FIGURE 3. Slurry bioreactor/land treatment pilot results.

percent. For the B720 soil the APC process reduced the TPH concentration from 340 mg/kg to 180 mg/kg, a reduction of 47 percent.

The performance of the APC process was hampered by the less rigorous soil conditioning which was used as compared to the SB/LT process. This was due to better soil conditioning with particle-size reduction, mixing, and deagglomeration of the duripan clods which was accomplished by the hammer milling and rod milling operations of the SB/LT process.

The less rigorous conditioning used for the APC process is also the primary cause of the erratic nature of the curves in



NOTE
ERROR BARS INDICATE STANDARD DEVIATION OF SAMPLES.

FIGURE 4. Aerated-pile composting treatment pilot results.

Figure 4. Because the soils were more heterogeneous in terms of particle size and contaminant distribution than the more rigorously conditioned soils of the SB/LT process, the sample results varied much more dramatically because of the more uneven initial TPH concentrations and treatment levels achieved throughout the piles. More rigorous soil conditioning would have provided more intimate contact between the contaminants, microorganisms, oxygen, water, and nutrients. Such soil conditioning would also have the effect of reducing the variability of soil monitoring data and reducing sampling and analysis costs.

Process Operability

The fine-grained nature of the soils and the abundance of duripan clods and cohesive silts and clays presented handling and operational challenges during operation of the conditioning equipment for the SB/LT process. One challenge involved soil bridging which occurred in the hoppers used during operation of the hammer and rod mills. Bridging is a term that describes plugging of an opening (such as at the bottom of a hopper) caused by adhesion of soil to itself and to the hopper, thus effectively stopping flow of material through the bottom of the hopper.

Another operational challenge resulted from the use of a belt feeder which was originally to be used to feed soil into the rod mill, but the soil tended to become compacted within the feed hopper, and the belt was not able to feed the soil continuously. The use of a screw-flight auger feeder was employed to overcome the shortcomings of the belt feeder. An additional challenge stemmed from the use of a jaw crusher to break some of the duripan clods. The clay in the clods plugged the crusher, making operation difficult. Also, because of a substantial amount of metal fragments, concrete, and other "debris" in the soil, special care was required during all operations to avoid damaging test equipment.

Another operational difficulty arose during the dewatering of the B720 and PL soil slurries following slurry bioreactor treatment. The difficulties began when polymer found to be effective for thickening and dewatering in the bench-scale solids handling studies was not effective with either of the soils used in the pilot study. This may have been due to slight differences in soil chemistry or differences in the solids processing used prior to dewatering testing. When these difficulties in the pilot study were noted, additional bench-scale thickening/dewatering tests were conducted on the soils being used during the pilot-scale tests. A different polymer (Percol 1011, a high-molecular-weight anionic polyacrylamide) was found to be effective under laboratory conditions in flocculating and thickening of the slurry. When this polymer was used in the pilot studies, flocculation occurred by the floc broke apart in the thickener. Consequently, it would appear that it is possible to flocculate these solids but that the floc is very delicate and breaks apart due to the physical action that occurs during thickening and dewatering.

The APC process was easier to operate, required less operations and maintenance (O&M), and was more robust with respect to varying soil characteristics than the SB/LT process. The slurry bioreactor used for the SB/LT process was found to be extremely sensitive to particle size distribution and water content. Given the highly variant soils that were encountered, this would be very difficult to control at full scale. In addition, the difficulties in dewatering the slurry likely render this technology infeasible for treatment of the soils at McClellan AFB.

Volatile Organic Compound Control

Both bioremediation systems provided a means of mitigating VOC emissions during soil treatment by inducing

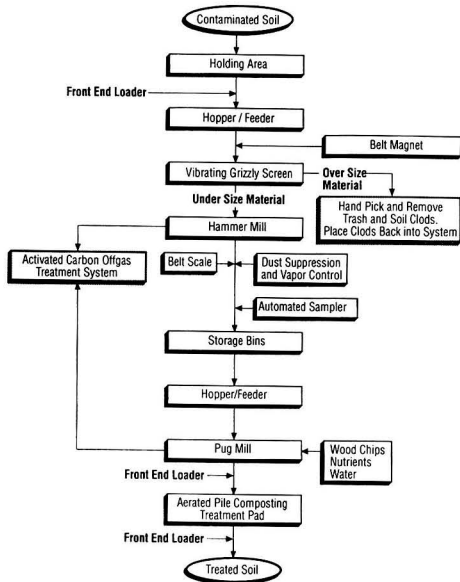


FIGURE 5. Full-scale treatment process.

volatilization and confining volatilized contaminants to an offgas stream that could be treated.

FULL-SCALE TREATMENT SYSTEM

The aerated-pile composting and slurry bioreactor/ex situ land treatment processes offered suitable treatment performance and the ability to control VOC emissions during treatment; however, the APC process was more robust with respect to variability in soil characteristics and generally required less O & M. Consequently, the APC process was used as part of a recommended full-scale treatment system for use at McClellan AFB. Figure 5 presents the process flow schematic for the recommended system.

Soil Conditioning

The system would begin with a holding area where the soil to be treated would be stockpiled and covered with tarps. If further characterization of soil contamination was required, samples would be collected from these piles for analysis. Soil from various sources would be segregated and treated separately unless the contaminant characteristics were similar or if mixing two soil types were deemed appropriate. A front-end loader would be used to transfer the soil from the stockpiles to a hopper/feeder which would feed the soil at a controlled rate to a conveyor belt having a magnet overhead to remove ferrous debris. This is important to protect the downstream process equipment.

The conveyor would feed a vibrating grizzly with nominal 2- to 3-inch (5.1- to 7.6-centimeter) openings which would remove the oversize rocks, clods, and debris. The oversize materials would be hand-sorted and the separated rocks and debris could be steam-cleaned if appropriate and discarded, and the oversize clods and agglomerates would be returned to the system for size reduction.

Undersize material from the grizzly screen would discharge directly into a hammer mill for size reduction. Dust control would be maintained at the hammer mill utilizing a

wet-surfactant spray system. The hammer mill would discharge to a conveyor system, which would transfer the material to a series of storage bins.

The bins would discharge by feeder to a conveyor which would transfer the soil to the pug mill where soil amendments such as wood chips, nutrients, and water would be mixed with the soil. The pug mill would discharge to a conveyor, which would convey the amended soil compost to a concrete pad to await transfer to the compost area by front-end loader.

Soil Treatment

The composting pad would be located adjacent to the mixing pad and would be divided into 14 treatment cells to segregate soils with different characteristics and to provide flexibility with respect to batch treatment startup and completion times. The pad would consist of a sandy clay base overlain with a PVC membrane. On top of the membrane would be a pea gravel drainage layer in which perforated pipe spaced every 2.5 meters would be embedded for the aeration system. The aeration pipes from under the piles would be manifolded and valved prior to connection with the blowers so the airflow through each could be regulated independently. A stabilized permeable base would overlay the pea gravel to provide a working surface. An extruded concrete curb would surround the pad to direct runoff toward a sump in the corner from which a pump would transfer the water to a holding tank. The water in the holding tank could be recycled onto the piles. The entire pad would be surrounded by an earthen berm to protect the curb from damage by the front-end loader.

The soil piles would be constructed using a front-end loader which would place uncompacted soil approximately 2 meters high by 4 meters wide by 15 meters long. Side slopes would be determined by the natural angle of repose of the soil. During construction of the soil piles, oxygen-monitoring tubes would be embedded in the piles, and a drip irrigation system would be laid over the soil to provide moisture. Once the soil was in place, the valves controlling the air lines in those cells would be opened to begin drawing air through the piles to provide oxygen for biodegradation of organic contaminants. Blower operation would be cycled on and off to reduce operating costs. After the soil was treated to acceptable levels, it would be removed using the front-end loader and stockpiled to await its end use.

Control of VOCs would be accomplished by maintaining a slight negative pressure on the exit ports of the hammer and pug mills. A hammer mill induces intimate contact between soil and air because air is drawn through the system as the soil particle size is reduced. A pug mill also induces VOC emissions through the mixing of soil with amendments. By taking advantage of the ability of these processes to induce volatilization of VOCs, the readily stripped compounds would be collected for treatment, thereby reducing VOC emissions during subsequent soil handling. The collected offgas streams from the hammer mill and pug mill would be conveyed to a vapor-phase granular activated-carbon system for VOC treatment. This same carbon treatment system would also be used to treat the aerated-pile composting offgas.

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Stripping of TCE from Water at Low Air/Water Ratios

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Trichloroethylene was removed from water by air stripping in a packed column using low air/water ratios, and the measured removal efficiencies were used to correlate the height of a transfer unit using a model which takes into account both liquid- and gas-phase resistance to mass transfer. The resulting correlation was used to optimize the design of a combined air stripper and offgas treatment system.

Estimated overall cost savings of up to 26% compared to conventional air strippers can be realized by use of the optimum air/water ratio.

INTRODUCTION

Air stripping is a cost-effective technology for removing a wide range of volatile organic compounds (VOCs) from contaminated groundwater. However, if the stripper offgas cannot be directly discharged, the cost of capturing the stripped VOCs can be a major part of the overall system cost. Systems for remediating contaminated groundwater typically use vapor-phase granular active carbon (VGAC) adsorption units to capture the stripped VOCs.

VGAC costs can be reduced by decreasing the air flow from the stripper. Since the water throughput is constant, lowering the air flow decreases the air/water ratio. A taller column is required to achieve the same percentage VOC

removal with a lower air/water ratio. Stripping towers in groundwater treatment applications are typically operated at volumetric air/water ratios between 20:1 to 300:1 [1]. Optimizing air stripping/VGAC groundwater treatment systems to minimize overall cost requires reliable data on VOC mass transfer efficiencies at air/water ratios less than those used in conventional systems.

This study provides data on air stripping of trichloroethylene (TCE) from water at air/water ratios ranging from 20:1 to 2:1. The results are used to evaluate alternative treatment systems for a hypothetical TCE-contaminated groundwater stream. The system cost estimates balance the decreased VGAC system size needed for offgas treatment against the increased column height required at lower air/water ratios.

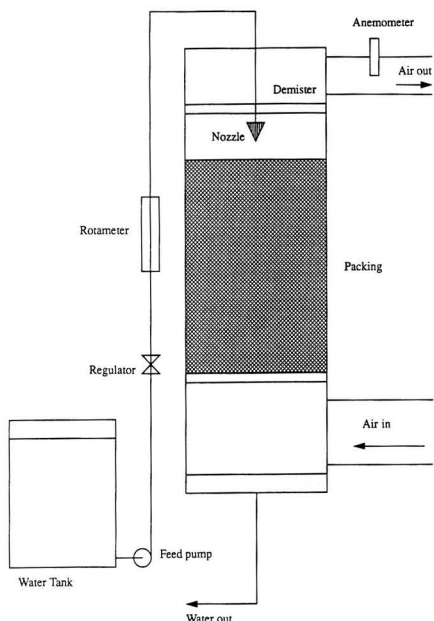


FIGURE 1. Air stripping apparatus.

EXPERIMENTAL

Methods and Materials

The experimental apparatus is shown schematically in Figure 1. A square Plexiglas column measuring 41 × 41 cm was packed with 152 cm of a commercial random dumped packing (polypropylene LANPAC^R, nominal size 5.8 cm). Water was distributed across the top of the packed bed by spraying from a spiral nozzle. Stripping air entered the bottom of the

column through a square duct equipped with a simple damper mechanism.

The flow rate of the air was determined by measuring its velocity with an anemometer as it passed through a 10.2-cm duct at the top of the column. The water flow was measured using a rotameter. Samples of water containing dissolved TCE were prepared by first pipetting 0.06 mL of TCE into the bottom of a 10-mL beaker of water. Because TCE is dense and poorly soluble in water, it sank to the bottom of the beaker, where droplets were visible. The beaker was then lowered into a 61 × 61 × 122-cm PVC tank as the tank was filled with water. Two turbine-blade electric mixers and the turbulence caused by the jet action of the water inlet hose were used to thoroughly disperse the TCE, allowing it to dissolve in the water over a period of 10 minutes.

The water was pumped through the stripping column at 68 or 131 L/min, and stripped with air at various flow rates, as shown in Table 1. During each run, the stripper was allowed to operate for 3 minutes in order to reach steady state before the inlet and outlet water streams were sampled. Samples were collected in 40-mL amber glass containers with PTFE-lined caps, with care taken to avoid air bubbles. The samples were stored at 2°C, and analyzed for TCE by EPA Method 502.2, using a gas chromatograph with a purge/trap unit, a Volcol 105 column, and a Hall detector.

RESULTS AND DISCUSSION

Air Stripping Studies

Experimental results are listed in Table 1. These were used to calculate the number of transfer units provided by 152 cm of packing.

The data measured at the lowest air flow rates have the greatest amount of experimental error, because the air velocity in the duct was near the lower limit of sensitivity of the anemometer.

The Henry's Law constant of TCE in water was calculated from the relation reported by Kavanaugh and Trussell [1]

$$\log_{10} H_{(\text{atm})} = 8.59 - \frac{3410 \text{ cal/mol}}{RT}$$

The *HTU* values for TCE stripping under the various experimental conditions were calculated and then plotted as a function of air flow rate. (See Figure 2). The broken lines show the *HTU* values predicted by the packing manufac-

Table 1 Experimental Results

Run No.	Water Flow Rate (m ³ /h)	Air Flow Rate (m ³ /h)	Water Temperature (°C)		TCE Concentration (ppb)	
			inlet	outlet	inlet	outlet
1a	7.83	18.5	19.0	19.0	126.3	55.2
1b	7.83	14.8	18.9	18.9	133.7	68.6
1c	7.83	14.8	18.6	18.4	125.3	101.0
2a	7.83	46.7	18.0	18.0	87.0	41.7
2b	7.83	46.7	17.7	17.7	136.5	61.1
3a	7.83	74.1	18.0	18.0	100.5	36.0
3b	7.83	70.5	17.6	17.6	137.1	40.1
4a	7.83	148.3	17.9	18.1	211.0	52.7
4b	7.83	140.8	18.8	18.9	176.4	46.9
4c	7.83	140.8	19.2	19.2	198.6	42.5
5a	7.83	214.9	18.9	18.7	136.5	32.6
5b	7.83	207.6	18.1	18.0	242.5	41.1
7a	4.09	22.3	18.1	18.2	216.6	71.9
7b	4.09	21.6	18.1	18.2	222.5	84.7
7c	4.09	22.3	18.2	18.3	164.0	59.2
8a	4.09	35.5	17.2	17.2	211.3	60.9
8b	4.09	34.2	17.1	17.2	239.2	70.3
9a	4.09	74.1	17.1	17.1	183.9	38.0
9b	4.09	74.1	17.2	17.2	224.3	44.1

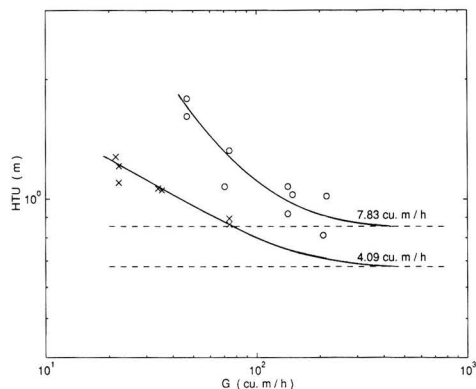


FIGURE 2. Experimental heights of a transfer unit for stripping of TCE.

Table 2 Alternate System Designs and Costs

	Design Parameters					
	5:1	10:1	15:1	20:1	30:1	50:1
Air/Water Ratio (m ³ /m ³)	5:1	10:1	15:1	20:1	30:1	50:1
Air Flow Rate (m ³ /h)	1580	3160	4740	6320	9480	15800
Adjusted HTU (m)	1.99	1.74	1.62	1.47	1.37	1.36
Packing Height (m)	17.5	9.3	7.8	6.7	5.9	5.6
Stripper Pressure Drop (Pa)	12	25	45	70	139	364
VGAC Bed Diameter (m)	1.2	1.5	2.0	2.3	2.7	2.7
VGAC Bed Carbon (kg)	514	803	1357	1807	2602	4626
	Capital Costs					
Stripping Tower (\$)	110,428	74,740	67,796	62,049	57,717	55,922
VGAC Unit (\$)	11,388	17,540	29,148	38,457	54,741	95,528
Carbon (@ \$3.85/kg)	1,979	3,092	5,226	6,958	10,021	17,812
Instrumentation & Controls (\$)	12,182	9,228	9,694	10,051	11,246	15,145
Taxes & Freight (\$)	9,745	7,382	7,755	8,040	8,997	12,116
Total Purch. Equip. Cost (\$)	145,723	111,983	119,619	125,555	142,721	196,523
Direct Installation Costs (\$)	71,404	54,872	58,613	61,522	69,933	96,296
Indirect Installation Costs (\$)	45,175	34,715	37,082	38,922	44,243	60,922
Total Capital Cost (\$)	262,301	201,569	215,314	225,999	256,897	353,741
	Operating Costs					
Operating Labor (\$/yr)	5,475	5,475	5,475	5,475	5,475	5,475
Maintenance (\$/yr)	5,246	4,031	4,306	4,520	5,138	7,075
Utilities						
Carbon Consumption (kg/yr)	903	1055	1158	1236	1355	1521
Carbon Replacement Cost (\$/yr)	3,475	4,062	4,458	4,759	5,219	5,857
Fan Power (kW)	1.88	3.78	5.70	7.66	11.76	21.00
Fan Electricity Cost (\$/yr)	1,303	2,617	3,951	5,312	8,149	13,799
Total Operating Cost (\$/yr)	15,499	16,186	18,191	20,065	23,981	32,462
Annualized Capital Cost (\$/yr)	39,083	30,034	32,082	33,674	38,278	52,707
Total Annualized Cost (\$/yr)	54,582	46,220	50,273	53,739	62,258	85,169
Treatment Cost (\$/m ³)	0.0203	0.0171	0.0188	0.0198	0.0230	0.0314
Cost Savings (vs. A/W = 30:1)	12%	26%	19%	14%	0%	-37%

turer's correlations, based on data from air strippers operating at $A/W \geq 20:1$.

Conventional air strippers typically are designed to operate with air/water ratios high enough so that the resistance to mass transfer is entirely in the liquid phase. Under such conditions, the height of a transfer unit is independent of the air flow rate. At low A/W ratios, however, the finite rate of contaminant transfer from the air/water interface into the bulk gas phase has an appreciable effect. This explains the increase in HTU seen at air/water ratios less than 20:1 in this experiment. The two-film model [2] of mass transfer predicts that the overall height of a transfer unit, where both liquid-phase and gas-phase resistances are significant, varies as

$$HTU_{OL} = HTU_L + \frac{P_T}{H} \frac{L_m}{G_m} HTU_G$$

where, L_m and G_m are the molar liquid and gas loadings (mol/h-m²), H is the Henry's Law constant, P_T is the total pressure, and HTU_G is the height of a gas-phase transfer unit.

Fitting the results to an equation of this form gives HTU_G values of 152 ± 30 cm. This result, although approximate, can serve as a guide for designing air strippers operating under comparable conditions at air/water ratios between 5:1 and 25:1.

Cost Analysis of a Hypothetical Groundwater Treatment System

The higher HTU values for a stripper using less air indicate that a greater packing height will be needed in order to compensate for the reduced rate of mass transfer. Thus, al-

though the use of low air/water ratios decreases offgas treatment costs, larger stripping columns are required to achieve the same removal efficiency. Eventually, as the air/water ratio is decreased sufficiently, the cost savings from smaller offgas treatment equipment is offset by the increased cost of the stripping tower. A hypothetical system to treat 7,570 m³/day of groundwater contaminated with 25 mg/L of TCE to drinking water standards (0.5 µg/L) is analyzed below to demonstrate how the total cost for an air stripping/VGAC adsorption system can be minimized based on the experimental results presented above.

Treatment system parameters and costs are summarized in Table 2. Cost estimating procedures, based on direct equipment capital costs as described in the EPA OAQPS Control Cost Manual and Vatauvuk (Estimating Costs of Air Pollution Control), were followed. Recent vendor quotes for equipment of the approximate size required for our example treatment system were used in estimating the equipment costs from which direct and indirect capital costs were factored. Typical liquid loading rates in groundwater stripping applications are in the range of 0.2-1.2 m³/min-m². A stripping tower 2.4 m in diameter, providing a liquid loading of 1.11 m³/min-m², was assumed. Carbon bed sizing is typically based on superficial air velocity through the bed of approximately 24-30 m/min. VGAC sizing was based on a superficial velocity of 27.4 m/min.

Operating costs were based on 0.5 hr/day operating labor at \$30/hr, maintenance at 2% of total capital cost, electricity based on fan power consumption only (\$0.075/kW-hr), and a carbon replacement cost of \$3.85/kg. The capital recovery cost factor of 0.149 used assumes a 10 year service life and 8% interest.

As can be seen from Table 2, a 26% cost savings could be realized by operating the system at an air/water ratio of 10:1 in comparison to a more typical air/water ratio of 30:1. For

this system, an air/water ratio of 10:1 minimizes total cost. Further decreasing the air/water ratio increases total cost from the 10:1 minimum due to the increase in stripping tower capital cost.

Summary and Conclusions

Stripping of TCE from water at air/water ratios less than 20:1 was investigated. Experimental results were used to calculate the *HTU* for use in sizing stripping towers. A cost analysis of a hypothetical system to treat TCE-contaminated groundwater showed that total treatment costs could be minimized by operating the stripping tower at an air/water ratio

below those typically used in existing systems. This study demonstrates the value of additional work to develop reliable correlations for estimating *HTUs* at air/water ratios where gas-phase mass transfer resistance is significant.

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Integrating Low-NO_x Burners, Overfire Air, and Selective Non-Catalytic Reduction on a Utility Coal-Fired Boiler

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Public Service Company of Colorado (PSCo), in cooperation with the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI), is testing the Integrated Dry NO_x/SO₂ Emissions Control System. This system combines low-NO_x burners, overfire air, selective non-catalytic reduction (SNCR), and dry sorbent injection with humidification to reduce by up to 70% both NO_x and SO₂ emissions from a 100 MW coal-fired utility boiler. The project is being conducted at PSCo's Arapahoe Unit 4 located in Denver, Colorado as part of the DOE's Clean Coal Technology Round 3 program. The urea-based SNCR system, supplied by Noell, Inc., was installed in late 1991 and was tested with the unmodified boiler in 1992. At full load, it reduced NO_x emissions by about 35% with an associated ammonia slip limit of 10 ppm. Babcock & Wilcox XCL[®] burners and a dual-zone overfire air system were retrofit to the top-fired boiler in mid-1992 and demonstrated a NO_x reduction of nearly 70% across the load range. Integrated testing of the combustion modifications and the SNCR system were conducted in 1993 and showed that the SNCR system could reduce NO_x emissions by an additional 45% while maintaining 10 ppm of ammonia slip limit at full load. Lower than expected flue-gas temperatures caused low-load operation to be less effective than at high loads. NO_x reduction decreased to as low as 11% at 60 MWe at an ammonia slip limit of 10 ppm. An ammonia conversion system was installed to improve performance at low loads. Other improvements to increase NO_x removal at low-loads are planned. The combined system of combustion modifications and SNCR reduced NO_x emissions by over 80% from the original full-load baseline.

PROJECT BACKGROUND

Public Service Company of Colorado (PSCo) is an investor-owned utility that serves Colorado and the surrounding region. PSCo has always striven to be an environmentally

responsible corporation and has been a leader in using fabric filter dust collectors (FFDCs) for particulate control.

PSCo's main fuel is low-sulfur Western coal. A comprehensive study of the Denver Metro area's pollution in the late 1980s showed that PSCo's coal-fired generating stations are

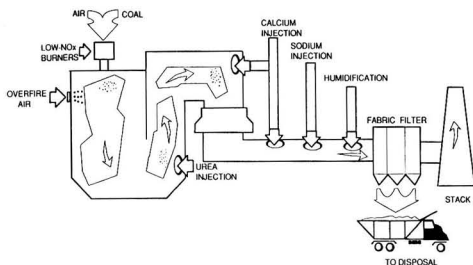


FIGURE 1. Integrated dry NO_x/SO₂ emissions control system.

responsible for less than 1% of the direct particulate that makes up Denver's famous brown cloud. The study, however, also found that secondary particulates of ammonium sulfate and nitrate contributed significantly to the brown cloud, but the study could not attribute these secondary particulates to any specific source.

As part of a voluntary program, PSCo began retrofitting its Denver-area boilers with low-NO_x (oxides of nitrogen) combustion systems and has now modified one wall- and two tangential-fired boilers with low-NO_x burners. PSCo also operates six top-fired pulverized coal boilers for which no combustion modifications are commercially available. PSCo decided to take a leading role in the development of NO_x reduction technologies for this unusual boiler type.

Integrated Dry NO_x/SO₂ Emissions Control System

PSCo proposed the Integrated Dry NO_x/SO₂ Emissions Control System to the U.S. Department of Energy (DOE) as part of the third round of the Clean Coal Technology Program (CCT-III). The proposed system was the first demonstration of low-NO_x burners, overfire air (OFA) ports, and urea-based selective non-catalytic reduction (SNCR) on a top-fired-utility-coal boiler. The integrated system also includes dry sorbent injection (DSI) using both sodium- and calcium-based reagents and flue-gas humidification to control sulfur dioxide (SO₂) emissions. Figure 1 shows a simplified schematic of the Integrated Dry NO_x/SO₂ Emissions Control System at Arapahoe Unit 4.

The DOE and PSCo signed the cooperative agreement for the Integrated Dry NO_x/SO₂ Emissions Control System in March 1991. Installation of the integrated system to Arapahoe Unit 4 was completed in August 1992 and testing will be completed in mid 1995. Remaining work includes the installation and testing of additional SNCR lances to improve SNCR performance at low loads. The program is scheduled to be completed by November 1995.

The program's overall goal is to achieve up to 70% reductions in the emissions of NO_x and SO₂ through the integration of existing and emerging technologies while minimizing capital expenditures and limiting waste production to dry solids that can be handled with conventional ash removal equipment. This innovative demonstration project is estimated to cost \$27,411,000. It is funded by the DOE (50.0%), PSCo (43.7%), and the Electric Power Research Institute (6.3%).

Unit Description

PSCo is conducting the Integrated Dry NO_x/SO₂ Emissions Control System project on Unit 4 at its Arapahoe Steam Electric Generating Station located in Denver, CO. Arapahoe Unit 4 is a top-fired unit rated at 100 MWe (megawatt-

electric). It was designed to burn pulverized coal (Colorado lignite) or natural gas and came on line in 1955. PSCo uses Arapahoe Unit 4 as a load-following unit; its normal capacity factor ranges from 50 to 60%.

B&W DRB-XCL® LOW-NO_x BURNERS

The original furnace configuration was a top-fired system that employed 12 intertube burners located on the roof and arranged in 1 row across the width of the furnace. Each burner consisted of a rectangular coal/primary-air duct split into 20 nozzles arranged in a 4-by-5 rectangle that injected the coal/air mixture evenly across the furnace roof. A secondary-air windbox surrounded each burner and allowed air to flow around each of the coal nozzles resulting in a checkerboard pattern of coal/primary-air and secondary-air streams. The burners had no provision to control the mixing rate of the fuel and secondary air.

The Integrated Dry NO_x/SO₂ Emissions Control System uses Babcock & Wilcox (B&W) Dual Register Burner-Axially Controlled Low-NO_x (DRB-XCL®) burners. The burners use air and fuel staging within the burner to reduce the formation of NO_x. They can also balance the distribution of fuel and air to each burner to optimize combustion efficiency and NO_x reduction. On wall-fired boilers, these burners have achieved NO_x reductions of 35 to 70% from uncontrolled baseline levels.

Modifying a top-fired boiler for low-NO_x burners needs more outage time, requires a larger capital investment, and is much more complicated than it is for a wall-fired boiler. The design of the original intertube-burners is not comparable to that of the more common wall-fired burners. Installing low-NO_x burners into a top-fired boiler requires the:

- Modification of the burner for vertical operation (DRB-XCL® burners are designed to be fired horizontally).
- Replacement of all roof tubes.
- Modification of ductwork for secondary air.
- Removal of any asbestos.
- Replacement of the windbox.
- Rerouting of coal and gas piping.
- Major modification of the control system.

Although Arapahoe Unit 4 mainly burns coal, it also fires natural gas occasionally to provide load when pulverizers or other equipment are out of service. A gas ring-header located at the tip of each burner maintains Arapahoe Unit 4's capability to fire 100% natural gas.

Overfire Air

OFA ports use air staging over a larger volume of the furnace than low-NO_x burners by diverting part of the combustion air from the primary combustion zone to a zone downstream of the burner. This diversion creates a slightly fuel-rich environment that inhibits the formation of NO_x. The Integrated Dry NO_x/SO₂ Emissions Control System uses B&W Dual-Zone NO_x Ports®, which incorporate a central (inner) zone and an outer zone to provide adequate mixing across the entire furnace.

Unlike wall-fired boilers, adding OFA ports to top-fired boilers involves more than a simple extension of the windbox. Instead, installing OFA ports into a top-fired boiler requires new ductwork to carry the OFA to the OFA ports. This additional ductwork must fit the existing unit and significantly increases the capital cost of installing OFA ports. When used with pulverized coal, OFA ports can increase slagging and corrosion in the furnace and decrease combustion efficiency.

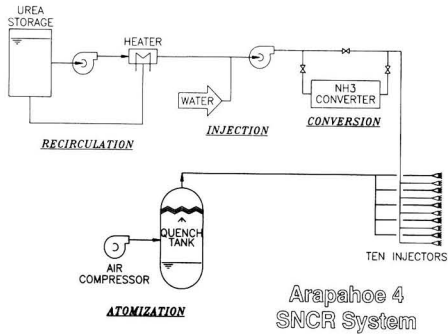


FIGURE 2. SNCR system.

SNCR (Urea and Ammonia Injection)

SNCR systems inject either urea or ammonia (anhydrous or aqueous) into the flue gas at a point where its temperature is between 1,600 and 2,100°F. In this temperature range and in the presence of oxygen (O_2), the injected chemical releases NH_2 which selectively reacts with NO and primarily forms harmless N_2 and H_2O . This reaction reduces NO_x emissions, but increases N_2O and NH_3 emissions.

Small changes in flue-gas temperature at an SNCR system's injection points can significantly affect its performance. When the boiler load is changed, the flue-gas temperature for a particular injection location also changes. For this reason, multiple levels of injection are usually required to provide good NO_x removal over a range of boiler load conditions.

Figure 2 shows a schematic of the SNCR system at Arapahoe Unit 4. The urea is diluted from 65 wt% to 37.5 wt% and stored in two tanks with a heated recirculation loop. The system diverts a small slipstream from the recirculation loop and pumps it at high pressure to the boiler. For low boiler loads, an on-line system uses a proprietary catalyst to convert the urea to ammonia compounds. The system then compresses air to medium pressure (4 to 12 psig) and injects the air and urea (or ammonia compounds) through 10 dual-fluid injection nozzles into the boiler. Based on tests performed before the combustion system was retrofitted (it was assumed that the low- NO_x combustion system would not significantly affect the exit temperatures of the flue-gas), two rows of injection nozzles were installed in the boiler—one row for boiler loads below and one row for loads above 80 Mwe.

RESULTS FOR LOW- NO_x COMBUSTION SYSTEM

The following section describes the reduced NO_x emissions of the low- NO_x combustion system (low- NO_x burners and OFA ports). Figure 3 compares the Arapahoe Unit 4's NO_x emissions before and after the retrofit of the low- NO_x combustion system. The original combustion system produced nearly uniform NO_x emissions of about 800 ppmc (parts per million corrected to 3% O_2 , dry) or 1.1 lb/MMBtu across the boiler's load range. The low- NO_x combustion system greatly reduced NO_x emissions to less than 300 ppmc across the boiler's load range. Note that all testing was conducted under steady-state conditions and the careful supervision of test technicians to achieve the maximum possible reduction in NO_x emissions for each system at Arapahoe Unit 4.

Results for Overfire Air

At full load, opening the OFA control dampers to full open (maximum OFA) diverts about 24% of the total com-

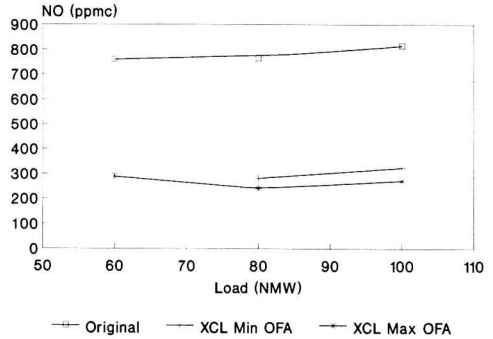


FIGURE 3. NO_x emissions before and after retrofit of low- NO_x combustion system.

bustion air to the OFA ports and at low load (60 MWe) it diverts about 28% of the combustion air. At maximum OFA, the low- NO_x combustion system reduced NO_x emissions by 62 to 69% across the load range. The OFA ports are located in a very hot part of the boiler and require a significant amount of cooling air. This requirement limits the minimum OFA to about 15% of the total combustion air at full load and to about 8% at low load. At minimum OFA, the low- NO_x combustion system reduced NO_x emissions by 60 to 63%. Arapahoe Unit 4 cannot be tested at 0% OFA, but the small difference in NO_x reduction between maximum and minimum OFA indicates that the low- NO_x burners are responsible for most of the NO_x reduction.

Although Figure 3 indicates that increasing from minimum OFA to maximum OFA reduced NO_x emissions by approximately 15%, the actual reduction due to OFA is believed to be less. The data shown in Figure 3 represents recommended operating points, but not at equivalent O_2 levels. As excess O_2 dramatically affects NO_x generation, the data cannot be directly compared. Tests of the low- NO_x combustion system show that Arapahoe Unit 4's NO_x emissions change by about 40 ppmc/% O_2 .

Figure 4 shows the effect of the OFA ports on NO_x emissions. The bottom line shows the NO_x emissions at maximum OFA, the same data shown in Figure 3. The top line shows the NO_x emissions at minimum OFA, but at a different excess O_2 level. The middle line shows the NO_x emissions at minimum OFA, but corrected to the same excess O_2 values as the maximum OFA data. As Figure 4 shows, the additional NO_x reduction that may be attributed to OFA is minimal.

At lower stoichiometric conditions, the OFA ports in Arapahoe Unit 4 may be too close to the burners to give suffi-

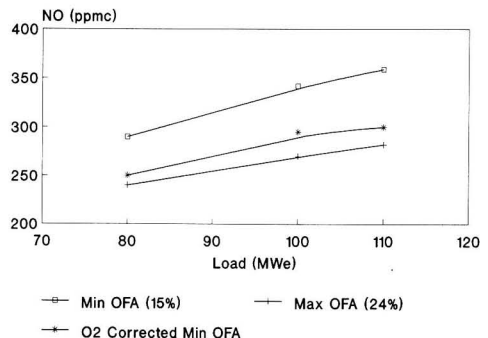


FIGURE 4. Effect of OFA ports.

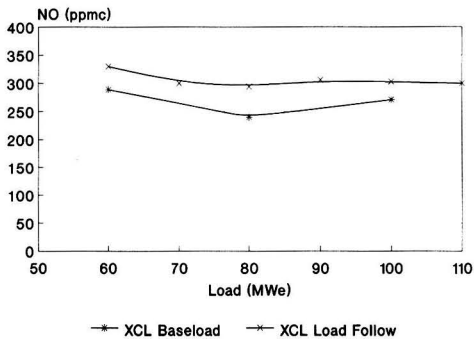


FIGURE 5. Load following NO_x emissions.

cient residence time and further reduce NO_x substantially. Unlike in wall- or tangentially-fired boilers, it appears that the low- NO_x burners in a top-fired boiler can control stoichiometry along most of the length of the boiler. This ability overlaps that of the OFA ports and minimizes their effectiveness at further reducing NO_x emissions.

Although OFA did not substantially improve NO_x reduction, it appears to reduce unburned carbon emissions and help maintain steam temperatures at low loads. Apparently, increasing OFA helps eliminate fuel-rich areas by improving the mixing of the flue gas and decreases both CO emissions and the amount of unburned carbon in the flyash. At low loads, increasing OFA appears to raise slightly the flue-gas temperature at the furnace exit, which increases steam temperatures.

Load Following Conditions

As Arapahoe Unit 4 is normally operated under automatic control as a load-following unit, Figure 5 compares the unit's NO_x emissions at constant loads under optimized test conditions to its NO_x emissions at varying loads under normal, load-following conditions. NO_x emissions under load-following conditions were about 10 to 25% higher.

Firing Natural Gas

A short test was also conducted of the low- NO_x combustion system firing natural gas. The low- NO_x burners were not designed to reduce NO_x while firing natural gas and the baseline NO_x emissions of the original combustion system firing natural gas are not available, so Figure 6 graphs the NO_x emissions at minimum and maximum OFA against excess O_2

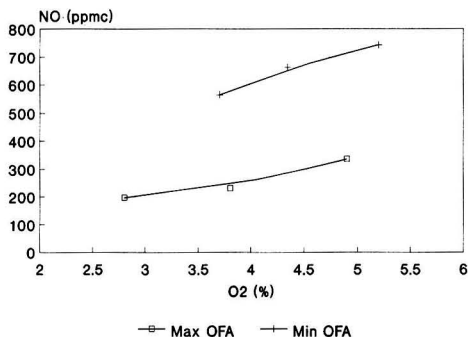


FIGURE 6. NO_x emissions firing natural gas.

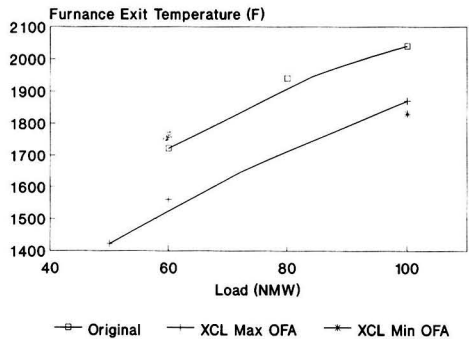


FIGURE 7. Flue-gas temperatures at furnace exit.

levels. At minimum OFA, NO_x emissions were slightly lower than those of the original combustion system firing coal. At maximum OFA, NO_x emissions were from 54 to 60% less than at minimum OFA (depending on excess O_2 levels) and comparable to those produced by firing coal at maximum OFA at similar excess O_2 levels.

The more rapid mixing of natural gas may account for the improved effectiveness of the OFA ports when firing natural gas. At equivalent excess O_2 levels, the low- NO_x combustion system's NO_x emissions were slightly higher when firing natural gas than when firing coal. However, as firing natural gas requires less excess O_2 to minimize carbon monoxide (CO) emissions, the low- NO_x combustion system can obtain slightly lower NO_x emissions (10 to 15%) firing natural gas instead of coal.

RESULTS FOR SNCR INJECTION

In addition to reducing NO_x emissions significantly, the low- NO_x combustion system also reduced the temperature of the flue gas at the furnace exit by about 200°F (Figure 7). As SNCR systems are very sensitive to changes in flue-gas temperatures, this reduction made the flue-gas temperature too cold for one row of injection nozzles, so all tests were performed using the row of injection nozzles originally designed for loads below 80 MWe.

NO_x Reduction

Figure 8 compares the NO_x reduction of the SNCR system at various stoichiometric ratios before and after the retrofit of the low- NO_x combustion system. At an ammonia slip limit

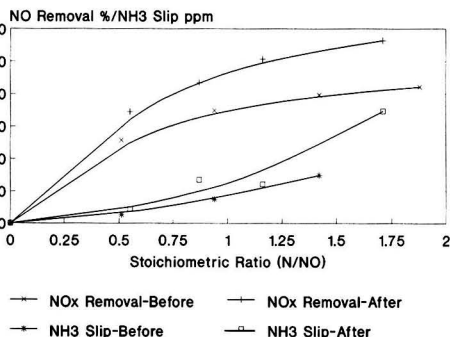


FIGURE 8. SNCR NO_x removal before and after retrofit of low- NO_x combustion system.

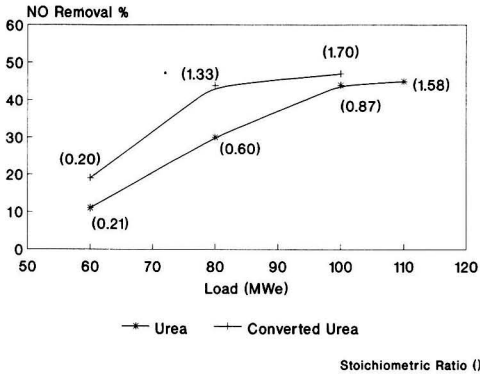


FIGURE 9. Comparison of NO_x reduction.

of 10 ppm, the SNCR system reduced NO_x emissions by about 37% with the original combustion system and by about 45% with the low-NO_x system. After the retrofit, the SNCR system required less urea to achieve the higher NO_x removal rate. It is believed that the increased efficiency is not related to the lower baseline NO_x levels of the low-NO_x combustion system, but rather to the decrease in flue-gas temperature at the injection location, as was shown in Figure 7.

Arapahoe Unit 4 is the first full-scale, coal-fired installation of SNCR that can inject either urea or ammonia. Figure 9 compares the NO_x reduction of urea and urea-converted-to-ammonia-compounds (converted urea) at an ammonia slip limit of 10 ppm. These results, however, depend on the slightly lower SNCR-temperature window of the converted urea and on the flue-gas temperature at Arapahoe Unit 4's injection location.

At 100 MWe, both chemicals achieve similar NO_x reductions, but urea is more efficient in terms of chemical utilization. At 80 MWe, converted urea achieves higher NO_x reduction, but still less efficiently. As Arapahoe Unit 4's load is reduced to 60 MWe, converted urea attains a higher NO_x reduction, and is more efficient than urea.

N₂O Emissions

In addition to ammonia slip, the use of SNCR can increase nitrous oxide (N₂O) emissions. Before the combustion system was modified, about 7 to 17% of the SNCR system's NO_x reduction appeared as N₂O emissions. After the combustion system retrofit, about 20 to 35% of the SNCR system's NO_x reduction appeared as N₂O, apparently because of the lower flue-gas temperatures.

Figure 10 compares N₂O generation as a percent of NO_x reduction at 60, 80, 100, and 110 MWe. While injecting urea, N₂O generation at 60 MWe is considerably lower than at 80 and 100 MWe. While injecting converted urea, there was much less N₂O generation, under 10%.

CONCLUSIONS

Figure 11 shows the total NO_x reduction achieved by the combination of the low-NO_x combustion and SNCR systems. From baseline NO_x emissions of about 800 ppmc, the low-NO_x combustion system reduced NO_x emissions by up to 69%, to under 300 ppmc. At an ammonia slip limit of 10 ppm, the SNCR system further reduced NO_x emissions by up to an additional 45%, to under 200 ppmc. The combination of both systems reduced NO_x emissions by over 80% at 100 MWe.

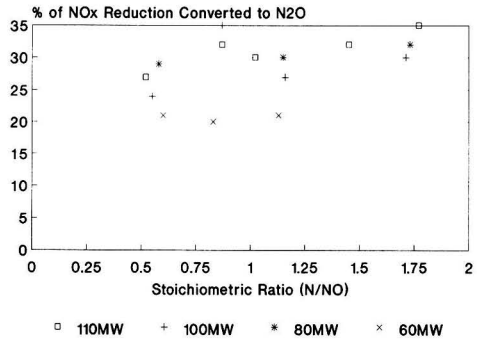


FIGURE 10. N₂O generation.

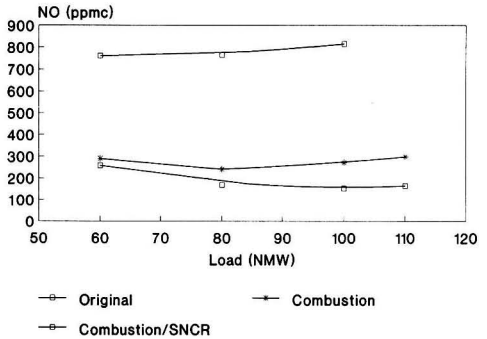


FIGURE 11. Combined NO_x emissions.

The low-NO_x combustion system could not be tested without OFA, but analysis indicates that the low-NO_x burners were responsible for most of the low-NO_x system's NO_x reduction on this top-fired boiler. Although the SNCR system alone did not achieve as high a level of NO_x reduction as expected, the combination of the SNCR and the low-NO_x combustion system, particularly the burners, exceeded expectations by reducing NO_x emissions by more than 80% from the original system.

ACKNOWLEDGEMENTS

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Results of a Two-Year *In Situ* Bioventing Demonstration

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A full-scale bioventing demonstration was recently completed at a large diesel spill site located at a major railroad facility in Nebraska. An estimated 11,500 cubic meters of soil are being treated in this demonstration. During this two-year demonstration, both in situ respiration rates and volatilization were routinely monitored to estimate total fuel removal rates. This paper discusses the relative contributions of biodegradation and volatilization in this bioventing application and presents two-year soil sampling results which indicate that significant fuel remediation has occurred at the site. Both capital and operating costs for this system are very competitive and will be detailed in this document.

INTRODUCTION

During early February of 1990, a ruptured pipe at a Burlington Northern Railroad (BNRR) fueling pump house in Nebraska resulted in over 230,000 litres of No. 2 diesel fuel spilling onto the surrounding soil. Several months later, a subsurface investigation indicated that soils were contaminated to a depth of approximately 20 meters. State regulatory agencies requested that BNRR develop and implement a remedial action plan to treat these diesel-contaminated soils and protect local ground waters. Parsons Engineering-Science, Inc. (ES) was retained for this work and, after evaluating a variety of remediation technologies, recommended using soil bioventing methods to begin the removal of volatile benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds and long-term biodegradation of all fuel residuals.

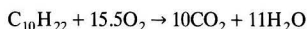
Parsons ES first designed and implemented a bioventing pilot test to determine soil properties such as air permeability, and to assess the potential for both volatilization and long-term biodegradation of diesel fuel residuals at the site. Pilot test results confirmed that bioventing was feasible for remediation of this site, and a full-scale bioventing system was installed on the site in September 1991. This system has operated continuously for over 30 months.

Fuel contamination in soil is often a long-term source of ground water contamination which must be addressed to en-

sure adequate site cleanup. A variety of *in situ* soil remediation options are now available for fuel-contaminated soils. The use of air as a medium to contact and remove volatile hydrocarbons has been extensively used in soil vapor extraction systems. Bioventing incorporates soil vapor extraction or air injection with the objective of supplying oxygen to subsurface bacteria to enhance fuel biodegradation. Initial bioventing research was completed by the Dutch scientist Van Eyk in the early 1980s [1] and by researchers at Chevron USA [2] and the U.S. Air Force during the late 1980s. A full-scale soil venting project to remediate a 100,000 litres JP-4 jet fuel spill at Hill Air Force Base (AFB), Utah was completed in 1989. During this 18-month project, jet fuel residuals in soils were reduced from an average total recoverable petroleum hydrocarbon (TRPH) concentration of approximately 900 milligrams per kilogram (mg/kg) to less than 5 mg/kg. Although this system was not optimized to reduce volatilization, monitoring of vented soil gas indicated that biodegradation accounted for at least 40 percent of the total removal [3, 4]. In 1991, Parsons Engineering Science, Inc. (Parsons ES) began commercial application of the bioventing technology and has now completed over 130 pilot and full-scale systems in 30 states.

Oxygen utilization rates measured during bioventing pilot tests have been used to estimate the rates at which fuel is biodegraded *in situ*. Complete biological mineralization of

fuel hydrocarbons (e.g., n-decane) can be described by the equation:



Approximately 3.5 grams of oxygen are required to completely mineralize 1 gram of fuel hydrocarbons to carbon dioxide [5]. This ratio actually underestimates fuel biodegradation because a third or more of the fuel hydrocarbons may be used in cell production rather than carbon dioxide production. A more realistic ratio is between 2.5 and 3.5 grams of oxygen utilized per gram of fuel hydrocarbon degraded.

In addition to oxygen supply, the distribution of petroleum-degrading bacteria and soil moisture conditions influence the success of *in situ* biodegradation. Active fuel degrading bacteria have been found in a wide variety of soil and climatic conditions and at depths of over 30 meters [6]. Extensive pilot testing conducted by the U.S. Air Force has also documented *in situ* biodegradation in soils with moisture levels ranging from 2 to 25 percent by weight. (Smaller bacterial populations and lower rates of biodegradation are associated with very dry soils. However, excessive soil moisture can cause a reduction in air permeability, limiting oxygen supply to soil bacteria.)

Soil bacteria also require a variety of nutrients to sustain hydrocarbon degradation. These nutrients, which include nitrogen, phosphorus, sulfur, and metals such as calcium and iron, are used by bacteria to synthesize new biomass and to manufacture enzymes. Soil bacteria must be able to obtain these nutrients from the subsurface environment. If nutrients are not available in adequate quantities, the growth of the bacterial population and the rate of hydrocarbon degradation may be limited.

In many fuel-contaminated soils, nutrients are available in adequate concentrations to support fuel biodegradation once oxygen is provided. Significant levels of biodegradation have been measured in soils with total Kjeldahl nitrogen (TKN) concentrations of less than 20 mg/kg and total phosphate levels of less than 3 mg/kg [6]. Bioventing research at Tyndall AFB, Florida indicated that soil bacteria are able to recycle essential nutrients, and may also rely on nitrogenase bacteria to fix atmospheric nitrogen and introduce useful forms of nitrogen for fuel-degrading microbes [7]. Attempts have been made to accelerate the biodegradation of petroleum hydrocarbons through the addition of nitrogen and phosphates. However, controlled nutrient additions at the Hill AFB and Tyndall AFB sites produced little increase in hydrocarbon degradation rates [3, 8].

SITE DESCRIPTION

The demonstration site is located at the Burlington Northern facility in Alliance, Nebraska, south of the diesel fuel pump house where the pipe rupture occurred (Figure 1). An estimated 11,500 cubic meters of soil has been contaminated to a depth of approximately 20 meters. In preparation for the pilot test, a single 4-inch (10.2-centimeter) vapor extraction well (VEW) and six 2-inch (5.2-centimeter) vapor monitoring points (VMPs) were installed at the site. Results of this pilot test have been reported in a previous publication [9].

Groundwater was observed at depths ranging from 20 to 21 meters below the surface. Intermittent lenses of perched water were also observed on the top of an interbedded sand, silt, and clay zone. BTEX compounds have been detected in groundwater; however, only benzene and total petroleum hydrocarbon concentrations exceed their respective cleanup goals of 5 micrograms per liter (mg/L) and 2 milligrams per liter (mg/L), respectively. The vast majority of the diesel fuel spill is adsorbed and occluded in the soil. Without soil treatment, soluble BTEX compounds will continue to migrate

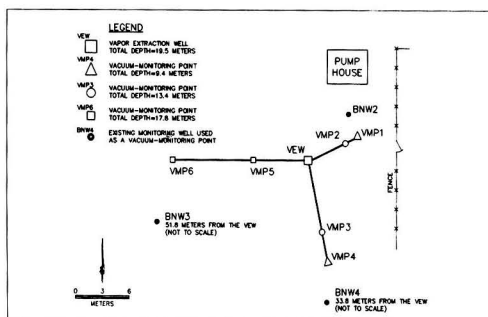


FIGURE 1. Site plan and monitoring point locations.

toward the groundwater creating a larger and more concentrated plume of contamination.

Soils at this site were characterized during construction of the VMPs and the VEW in April 1991. The general lithology in this area, shown in Figure 2, consists of fine- to medium-grained, silty sands from the ground surface to approximately 9.1 to 10.7 meters below ground surface (upper sand zone), interbedded sand and silt/clay lenses that extend 10.7 to 15.2 meters below ground surface (interbedded zone), and another layer of fine- to medium-grained silty sand that extends to a depth of 21.3 to 22.9 meters (intermediate sand zone). Soil moisture varied from 2 percent in the intermediate sand to 11 percent in the interbedded silts and clays.

Soil gas permeability was quantified through vacuum response tests conducted as part of the pilot test in April 1991 [9]. Vacuum response and oxygen concentrations were meas-

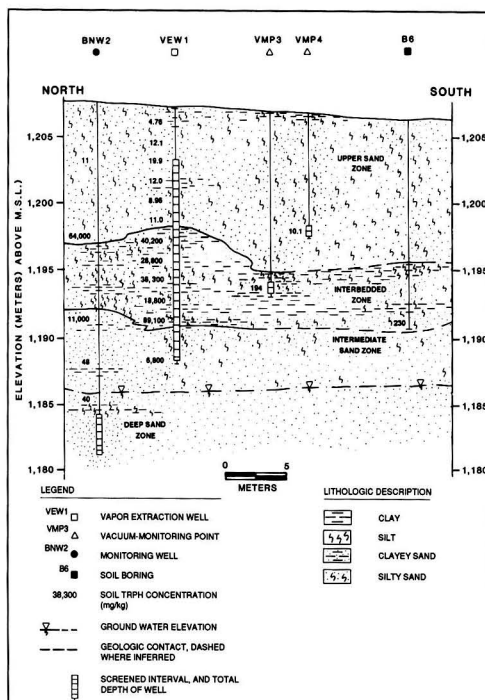


FIGURE 2. Geologic section.

ured at the VMPs and nearby monitoring wells (Figure 1), while soil gas was extracted from the VEW using a 10-horsepower (hp) vacuum blower. The soil responded rapidly to the vapor extraction system, with a measurable vacuum response and increases in oxygen concentrations occurring in all soil zones, including the interbedded silt/clay zone. Based on the radius and intensity of vacuum influence, the average soil gas permeability was estimated at 5 darcys. Because the contaminated soil zone was entirely oxygenated using the soil gas influx from a single VEW, the pilot VEW was adequate for full-scale remediation.

The diesel fuel contamination in the soil appears to be localized within a 20-meter radius of the pumphouse. Soils were analyzed using EPA Method 418.1 for TRPH. TRPH concentrations are plotted on the geologic section shown in Figure 2. Based on initial soil analysis, and observations made during drilling, it appears that diesel fuel migrated rapidly downward at the spill site until it encountered the interbedded sand and silt/clay zone at approximately 9.1 to 10.7 meters. At this depth, the fuel spread laterally and continued its downward movement through more permeable sand lenses in the interbedded layer.

Initial soil samples collected from the screened intervals of VMP4 and VMP5 were also analyzed for ammonia- and nitrate-nitrogen, TKN, and water-soluble phosphates. These analyses were performed to determine the concentrations of naturally occurring nutrients available in the soils. Ammonia-nitrogen was found at concentrations of 204 parts per million (ppm) in the upper sand zone (VMP4) and 4.2 ppm in the intermediate sand zone (VMP5), while nitrate-nitrogen levels ranged from 4 ppm in the upper sands to 11 ppm in the intermediate sand zone. TKN levels were found to be 4 ppm in both sand zones. Water-soluble phosphate concentrations ranged from 177 ppm in the upper sands to nearly 6,000 ppm in the intermediate sands. The relatively low nitrogen concentrations found in these soils may be limiting biodegradation rates. To determine if nitrogen addition could improve natural biodegradation rates, an ammonium nitrate solution was added to several VMPs after several months of bioventing. The results of this experiment are briefly described in the results section.

FULL-SCALE DESIGN, OPERATING, AND MONITORING

Based on the air permeability and oxygen influence observed during the pilot test, an extraction rate of 2.8 standard cubic meters per minute (m^3/min) was selected for full-scale bioventing operations. A 7-hp regenerative blower was required to produce this flow rate. Extraction from the central vent well was selected over air injection because of the immediate need to remove volatile and soluble BTEX compounds from the soil before further groundwater contamination occurred. The six VMPs established for pilot testing continue to be used to monitor vacuum response and to ensure that aerobic conditions are maintained throughout the contaminated soil volume.

The full-scale bioventing system has operated continuously for over two years with minimum maintenance downtime. BNRR personnel have been responsible for weekly system checks, monthly blower filter changes, and for monthly monitoring of oxygen and carbon dioxide concentrations in the extracted soil gas. At 6-month intervals, a Parsons ES engineer or technician has inspected the system and performed an *in situ* respiration test to estimate the level of fuel biodegradation occurring near each VMP. A sample of the soil gas extracted at the VEW is also sent to a certified laboratory for BTEX analysis.

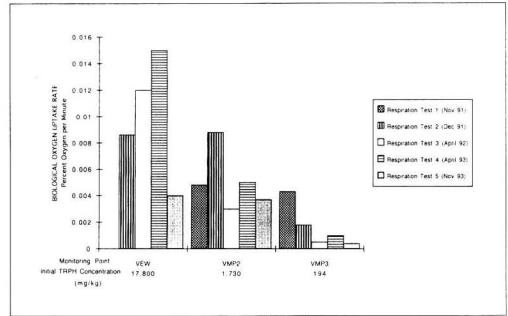


FIGURE 3. Biological oxygen uptake during respiration tests.

RESULTS

In Situ Respiration Testing

The fuel-consuming capability of native soil bacteria has been examined during four *in situ* respiration tests. Continuous soil vapor extraction creates an influx of oxygen-rich soil gas from surrounding clean soils. This continual supply of fresh soil gas provides the necessary oxygen for aerobic biodegradation. When the blower is turned off, soil gas influx stops and soil bacteria consume the available oxygen. Oxygen consumption and carbon dioxide production are monitored at each VMP using a portable O₂/CO₂ gas analyzer. The rate at which soil bacteria consume oxygen is an important indicator of the viability of the fuel-degrading organisms in soils near each VMP. Uncontaminated background VMPs were also monitored during the initial respiration test. Oxygen levels at these background VMPs remained relatively constant at approximately 18 percent, indicating that biological oxygen consumption of natural (nonfuel) organic carbon and abiotic oxygen consumption were not significant in these soils.

The results of respiration tests at VMPs 2 and 3 and the VEW are shown in Figure 3. Results indicate that in soils with low initial TRPH levels, the apparent rate of oxygen utilization has significantly decrease over time. Soils with higher TRPH levels have maintained higher oxygen utilization rates. Because larger bacterial populations are present in more contaminated soils, more rapid oxygen consumption has been observed. Very low rates of respiration have been measured in VMP 3 during the past two tests, indicating that little fuel is now available for biodegradation near this monitoring point. Recent soil sampling at VMP 3 confirmed that TRPH levels have been reduced from 194 mg/kg to less than 6 mg/kg.

Using a conservative range of 2.5 to 3.5 grams of oxygen utilized for every 1 gram of hydrocarbon degraded, the fuel biodegradation rate can be estimated for soils immediately surrounding the VEW and each VMP. Using this estimation method, the average biodegradation rate at the center of the spill (near the VEW) has been between 3,400 and 4,800 milligrams of TRPH degraded per kilogram of soil per year. Based on these average biodegradation rates the average concentration of diesel contamination should have been reduced by approximately 6,800 to 9,600 mg/kg over the two-year demonstration period.

In order to test the potential impact of additional nitrogen on *in situ* respiration rates, ammonium nitrate solution was added to VMPs 1, 2, and 3 immediately following the November 1991 respiration test and 3 weeks before the December 1991 respiration test [10]. Approximately 1.2 cubic meters of a 2,000 mg/L ammonium nitrate (as nitrogen) solu-

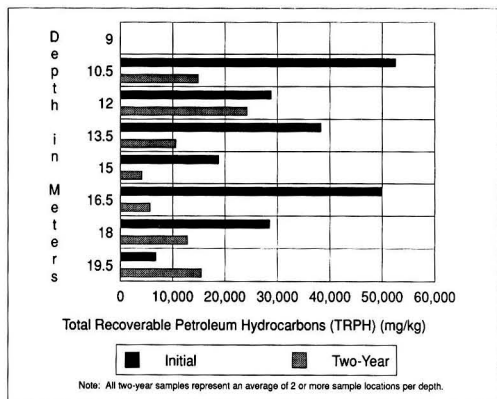


FIGURE 4. Two-year TRPH reduction during the full-scale bioventing demonstration.

tion was added to each VMP to ensure that a large soil volume near each VMP was supplied with nitrogen. Following nitrogen addition, a 25-percent increase in respiration rate was observed in VMP 1, and a 90-percent increase was observed in VMP 2. The test was not entirely conclusive because an unexplained decrease in respiration occurred in VMP 3. Also, because nutrients were applied using an aqueous solution, some of the increase in respiration may have been the result of improved moisture conditions.

Volatilization

The removal of volatile and water-soluble compounds such as BTEX from this large diesel spill is a key objective of this remediation project. Regular sampling of extracted soil gas indicated that an average of 0.3 kilograms of BTEX and 14.7 kilograms of diesel vapors have been removed during each day of bioventing operations. During the past two years an estimated 10,700 kilograms of total volatiles were removed by the bioventing system. Based on the estimated contaminated soil volume of 11,500 cubic meters, volatilization could account for an approximate 600 mg/kg reduction in soil TRPH.

Two-Year Soil Sampling Results

In order to more accurately assess remediation progress, soil samples were collected in early November 1993 at several locations and multiple depths and analyzed for TRPH using EPA Method 418.1 and BTEX using EPA Method SW8020. A total of 18 samples were collected from four borings in the center of the spill and within 6 meters of the vent well. This area was selected for sampling because it represented the most contaminated portion of the site based on initial soil sampling results. Figure 4 illustrates the general reduction in diesel concentrations from initial April 1991 levels. These soil samples indicate that an overall TRPH reduction of 55 to 60 percent has occurred over the past two years of bioventing. Only the 20-meter depth showed an apparent increase in fuel concentrations. This increase is likely due to the downward migration of the fuel. Selected soil samples were analyzed for BTEX compounds. A maximum total BTEX concentration of 73 mg/kg was detected. Benzene was present but at concentrations below the practical quantitation limit of 200 µg/kg.

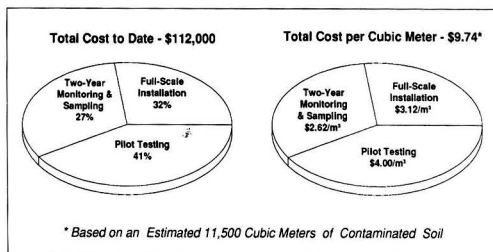


FIGURE 5. Cost summary for two-year bioventing demonstration.

CONCLUSIONS

Full-scale bioventing at this diesel spill site has produced encouraging results during the first two years of operation. Remediation is taking place throughout a 20-meter soil profile with no disruption to railroad operations or facilities. Recent soil sampling results indicate that a 55 to 60-percent decrease in diesel concentrations has occurred in the most contaminated portion of the site during the two-year demonstration. To date, over 90 percent of this removal can be attributed to *in situ* biodegradation, while volatilization accounts for less than 10 percent of the total hydrocarbon removal. There has been sustained oxygen utilization in the most contaminated soil volume and a significant decrease in respiration rates in soils with low initial TRPH concentrations. This reduction in respiration rates could indicate a significant reduction in hydrocarbons available for biodegradation near these points. The continuing removal of BTEX compounds in the extracted soil gas is reducing the potential of these compounds to enter the local aquifer. During the first two years of operation, an estimated 220 kilograms of BTEX have been removed from the spill area. Recent soil sampling indicates that low levels of BTEX remain in the soils.

The total cost to date of bioventing at this site including pilot testing, full-scale installation, and two years of operation and maintenance has been less than \$10 per cubic meter. Figure 5 shows a breakdown of total cost and a cost per cubic yard based on an estimated contaminated soil volume of 11,500 cubic yards. These totals include all Parsons ES costs, but do not include electrical costs or BNRR labor costs for system checks. The monthly electrical cost for the system is estimated at approximately \$280. Because bioventing provides a significant economy scale at this site, these costs should only be applied to sites with soil volumes exceeding 7,500 cubic meters. Bioventing costs for smaller sites are typically in the \$10–30/cubic meter range.

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Stormwater Management in Industrial Facilities: An Integrated Approach

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Numerous existing and proposed regulations have forced owners/operators of industrial facilities to reevaluate current methods for management of stormwater which falls within the confines of their facilities. Most have found it necessary to integrate their current stormwater and wastewater management practices into a comprehensive environmental compliance program. The development of an integrated stormwater management program should focus on the following objectives:

- *compliance with state and federal regulations*
- *the minimization of the volume of stormwater requiring treatment.*
- *the minimization of the impacts on process/production unit operations*
- *the minimization of the impacts on wastewater treatment unit operations.*

A well designed and properly implemented stormwater management program can reduce capital and operating costs and enhance effluent quality.

INTRODUCTION

The development of a stormwater management program that can be readily and effectively integrated into the overall environmental management plan for a facility can be expensive and complex. The implementation of such a program should address the specific requirements associated with stormwater management, as well as the mutual requirements of plant operations and associated environmental programs. The following project implementation profile has been developed to address the concerns mentioned above:

- Design Philosophy Development
- Management System Options Development
- Detailed Management System(s) Evaluation
- Project Implementation

The most crucial elements of this project approach are the first three phases, as they form the basis for, and can drastically affect the implementation of, the subsequent phases of the project. This paper will focus on these developmental phases

of the project and will only briefly discuss project implementation.

DESIGN PHILOSOPHY DEVELOPMENT

The first stage in the development of a stormwater management program, or any engineering project, is the development of a design philosophy. This phase of program development should focus on defining the problems to be addressed, gaining an understanding of the existing systems, and determining the overall objectives, both regulatory and design, to be employed in the subsequent phases of the project. The major elements associated with the development of a design philosophy for stormwater management programs should include:

- Regulatory Requirement Assessment
- Facility Audit
- Area Definition Map

The regulatory assessment results in the establishment of the regulatory compliance objectives to be addressed in the project design philosophy. The facility audit addresses the problem definition and existing system evaluation objectives of this project phase. The culmination of this phase of the project is the development of an overall plan drawing of the facility, the area definition map, which depicts the design philosophy to be adopted by the subsequent phases of the project.

Regulatory Requirement Assessment

Because state and federal regulations are generally the catalysts that compel owners/operators of industrial facilities to reevaluate and modify their existing stormwater management practices, it is essential to assess the applicability of those regulations when developing the design strategy. Regulations which affect stormwater management in industrial facilities include, but are not limited to, the following:

- EPA National Pollution Discharge Elimination System Permit Regulations (40 CFR 122)
- EPA General Provisions for Effluent Guidelines and Standards (40 CFR 401)
- EPA Resource Conservation and Recovery Act (40 CFR 260 to 266)
- Federal and State Water Quality Standards

When assessing regulatory requirements related to stormwater management, it is important to first determine which regulations apply to the specific industry with which a facility is associated (i.e., petroleum refining or chemical manufacturing). Once the comprehensive list of pertinent regulations has been compiled, the sections/subsections of these regulations that are applicable to the specific facility must be identified.

These specific requirements are then applied to the individual components of the existing stormwater and wastewater management systems at the facility. In most cases, individual companies which operate industrial facilities have adopted their own interpretations and regulatory compliance requirements. These facility interpretations/requirements are combined with the results of the regulatory review described above, and the regulatory compliance objectives for the project are developed.

In general, the regulatory compliance objectives for a stormwater management program include definitions which classify the waters which are discharged from a facility. The following key definitions have been employed on past projects:

- Process Wastewater—"... any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, by-product, or water product." [1, 2]
- Stormwater—"... storm water runoff, snow melt runoff, and surface runoff and drainage." [1]
- Stormwater Discharge Associated with Industrial Activity—"... the discharge from any conveyance which is used for collecting and conveying storm water and which is directly related to manufacturing, processing or raw materials storage areas at an industrial plant..." [1]
- Best Management Practices (BMPs)—"... BMPs also include treatment requirements, operating procedures, and practices to control plant site runoff, ..." [1]
- Contaminated Runoff—"The term 'contaminated runoff' shall mean runoff which comes into contact with any raw material, intermediate product, finished product, by-product or waste product located on petroleum refinery property." [2]
- Non-contaminated Runoff—Stormwater discharges from parking lots and administrative buildings along with other discharges from industrial lands that do not meet the regulatory definition of "associated with industrial activ-

ity" can be treated as "clean stormwater" or non-contaminated runoff.

Facility Audit

In order to determine the implementation strategies required to achieve the regulatory compliance objectives, it is often necessary to perform a detailed evaluation (audit) of the existing facility. The facility audit is an essential element in project definition and design philosophy development. The facility audit consists of an onsite investigation that can include any or all of the following tasks, depending on the size and scope of the project:

- Evaluate existing stormwater management system(s)
- Evaluate current operating, maintenance, and spill prevention and control procedures
- Review facility general environmental guidelines and design standards
- Collect/review existing stormwater system data
- Review existing discharge permit limits
- Identify potential sources of stormwater contamination
- Identify non-stormwater discharges
- Identify/review ongoing projects which may impact stormwater management

The results of this evaluation are utilized to develop a facility watershed map and a flow schematic that together depict the existing stormwater and wastewater management systems.

Area Definition Map

The final step in the design philosophy development phase of a stormwater management program is the development of what is referred to as an area definition map. The area definition map incorporates the regulatory definitions related to the stormwater and wastewater management systems and the findings of the facility audit into one comprehensive drawing. This map delineates the facility's watersheds into area classifications as set forth by the regulatory definitions. In previous projects, these area definitions included the following broad categories:

- Process areas—areas within the facility in which the manufacturing or processing of any raw material, intermediate product, finished product, by-product or waste product takes place.
- Contaminated areas—areas within the facility such as tank farms, product storage areas, material handling areas, lay down yards and other areas that are associated with an industrial activity but not directly associated with manufacturing or processing.
- Clean areas—areas within the facility which are not associated with industrial activity; where there is little or no potential for contamination of stormwater under normal operating conditions.

The area definition map can be further subdivided into more specific subcategories as required at each facility.

MANAGEMENT SYSTEM OPTIONS DEVELOPMENT

At this point in the project development, potential stormwater management options and a conceptual design basis can be developed. The two major concerns of any stormwater management program are the transportation (conveyance) and the storage (impoundment) of the stormwater which falls within a facility. There are several methods for analyzing stormwater

systems to determine the peak runoff rates and runoff volumes required to design stormwater conveyance and impoundment systems.

Storm Event Selection

A key element in estimating runoff rates and volumes is the selection of storm events to be utilized in the analyses. Statistical rainfall data, such as is published in the National Weather Service's Technical Paper No. 40, are typically used in runoff analysis.

Existing regulations provide little guidance in the selection of storm events for the design of stormwater management facilities. Storm events with durations equivalent to the time of concentration of a watershed are utilized to determine the peak runoff rates used to size stormwater conveyance systems. The duration of these storms is usually short, 10 minutes to 1 hour, because the watersheds being analyzed are small. Longer duration storm events, typically 24 hours, are used to determine the volume of stormwater requiring impoundment. During the options development phase of a project, storm events with return frequencies between 1 and 10 years and between 10 and 100 years are generally utilized to size the conveyance and impoundment systems, respectively.

Stormwater Management System Alternatives

The alternatives for management of stormwater vary depending on the regulatory compliance objectives and the layout and configuration of the existing stormwater and wastewater management facilities. The development of stormwater management system alternatives should consider the following general concepts:

- Source control and waste minimization to eliminate or reduce the amount of pollutants entering the stormwater system
- Segregation of process, contaminated or potentially contaminated areas from clean stormwater systems, wherever practical
- The minimization of contaminated/potentially contaminated stormwater volumes through the use of stormwater controls, such as:
 - installation of curbs or containment levees
 - modification of existing drainage barriers, (i.e., raising perimeter roads or levees)
 - modification/improvement of existing drainage patterns
- Addition of lift station and impoundment facilities to control the discharge of stormwater to the wastewater treatment facility, and
- Local impoundment of contaminated/potentially contaminated stormwater in product storage and tank farm areas during storm events.

In most cases, several options can be developed employing one or more of the concepts presented above. A preliminary evaluation of the options is performed to narrow down the field of potential candidates. Rudimentary hydrologic analyses, usually employing the Rational Method, are conducted to develop initial conveyance and impoundment system designs for the various options. This analysis is usually performed using several storm events to develop a matrix of sizing criteria for each option (i.e., varying storm duration and return frequency).

The options are then evaluated with regard to the following criteria:

- Constructability
- Operability

- Environmental and Safety Concerns
- Operating and Capital Costs
- Implementation Schedule

In most cases, this evaluation becomes an iterative one. The conceptual design basis and area definitions may require some fine tuning once the first run through the options evaluation process has been completed. The list of candidate options is then narrowed, and one or more feasible options is recommended for further detailed evaluation.

DETAILED MANAGEMENT SYSTEM(S) EVALUATION

The selected option(s) is then subjected to a more detailed analysis for refinement of the various elements of the management system. This analysis usually consists of modelling of the stormwater management system to predict peak runoff rates and runoff volumes.

Computer Modelling

For smaller watersheds where modifications to the drainage area and conveyance systems are not complex, straight forward analyses using the Rational Method may suffice. When major modifications to the drainage area (i.e., curbing and paving) and modifications to the conveyance system (i.e., installation of new interceptor sewers and lift stations) are proposed, a more detailed model should be considered.

The selected model should be capable of the following:

- simulating the runoff from a watershed for any prescribed rainfall pattern
- routing the runoff through the conveyance system
- simulating pressure flow or surcharge, backwater conditions, flooding, transfer of flow by weirs, orifices or pumping facilities and on- or off-line storage facilities
- simulating large sewer systems with large numbers of sub-catchments (watersheds), channels/pipes and junctions

The stormwater model which has been utilized in past projects is the United States Environmental Protection Agency Storm Water Management Model (SWMM).

At this point in the analysis, the storm events to be simulated are selected. For modelling the conveyance system, a statistical storm event with a return frequency of 10 years is typically selected. As stated previously, the duration of the storm event will vary depending on the time of concentration for the watershed(s) being modelled so that peak runoff rates can be determined. Less intense storm events of longer duration, typically a 25-year, 24-hour event, are simulated to determine stormwater impoundment volume requirements.

The outputs of the SWMM model include inflow hydrographs at selected inlets, outflow hydrographs at specified junctions, and conduit and junction output summary tables which include the location and duration of flooding in the system. The outflow hydrograph from the peak runoff analysis is then utilized to size the stormwater transfer system (lift station and pumps). The outflow hydrograph from the simulation of the 24-hour storm event is used to size the stormwater impoundment system.

The output from the peak runoff simulation is also evaluated to determine the location and duration of localized in-plant flooding. This is an important evaluation as the occurrence of flooding may adversely affect plant operations. If the flooding in some areas proves to be unacceptable, the conveyance system sizing (channels/pipes and/or transfer pumps) should be modified and the simulation rerun.

At the conclusion of the storm event simulation, storm sewer modifications, equipment and impoundment system sizes are defined and capital and operating costs are developed.

Risk Assessment

The system option(s) should at this point be subjected to a risk assessment. This risk analysis should address such items as events which exceed design capacity, equipment failure and operation errors. The results of this analysis may lead to modification of the design basis and the area definition map.

Selection of Management Program and Design Parameters

At the conclusion of the management system option(s) analysis, one stormwater management system, and its associated design basis is selected for design and construction.

PROGRAM IMPLEMENTATION

Having finalized the developmental phases of the stormwater management program, the next step is the refinement and implementation of the program through the following project phases:

- System Design Package
- Detailed Design Engineering
- Construction

The details of the project implementation phases of a project are more site specific than the development phases, so only a brief discussion of these phases will be presented.

System Design Package

The development of a system design package for the stormwater management system would include: design basis, P&IDs, equipment data sheets, tank data sheets, instrument data sheets, operating philosophy and instrumentation/control philosophy. This provides a refinement of the system design sufficient to:

- Develop a cost estimate of sufficient detail to support an appropriations funding request.
- Develop an implementation sequence for determining cash flow projections.
- Develop a construction/implementation schedule, recognizing continued operation of plant production facilities.

Detailed Design Engineering

Following completion of the system design package, the detailed design effort must proceed with production of construction drawings and specifications. Further refinement of the system design is expected to occur through such activities as pilot trenching of proposed sewer routings, final selection of equipment, sub-surface investigations, etc.

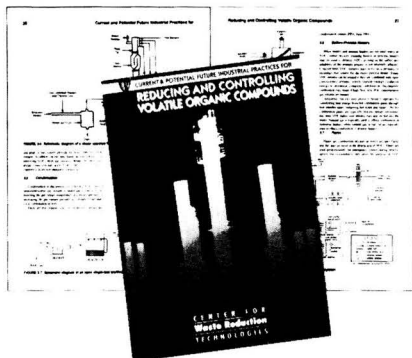
The environmental sensitivities which were established in the development phases of the project should be maintained by the continued participation of the original project team throughout the detailed design and construction phases.

Construction

The selection of a construction contractor and construction scheduling/sequencing must recognize the need to maintain the operation of both the plant production facilities and the waste treatment facilities throughout the construction period.

LITERATURE CITED

1. "EPA National Pollution Discharge Elimination System Permit Regulations," Code of Federal Regulations, Title 40—Protection of the Environment, Subchapter D, Part 122.
2. "EPA General Provisions for Effluent Guidelines and Standards," Code of Federal Regulations, Title 40—Protection of the Environment, Subchapter N, Part 401.



CWRT Announces A New Study On VOC Reduction Technologies

“Current and Potential Future Industrial Practices for Reducing and Controlling Volatile Organic Compounds”

Authors: Edward C. Moretti and Nik Mukhopadhyay, Baker Environmental, Inc.

Industries' and government's renewed interest in environmental issues is focusing attention on reducing and controlling volatile organic compounds. To meet this need, CWRT has published a new study on waste reduction technologies—"Current and Potential Future Industrial Practices for Reducing and Controlling Volatile Organic Compounds."

This important study evaluates existing and emerging "end-of-pipe" abatement technologies and air regulations, and offers an insightful economic analysis of selected abatement technologies.

Three abatement technologies were selected for detailed economic analysis: Thermal oxidizers and carbon adsorption systems were chosen because they are expected to continue to be the most popular choices throughout the decade, while biofiltration systems are expected to gain widespread acceptance.

This study is essential reading for those who make and market VOC control equipment, those who implement abatement programs and legislators and environmental regulators.

Manufacturers and marketers of VOC control equipment will find valuable customer information on what materials VOC emitters need to comply

with pending regulations. Data is also included on expenditures projected over the next five years.

Companies implementing abatement programs will find helpful data on emerging technologies that may radically change the application and treatment of VOCs in the near future.

Legislators and environmental regulators can use this study in establishing new standards and deadlines that are within the capabilities of VOC abatement technologies.

This study was commissioned by AIChE's Center for Waste Reduction Technologies and conducted by Baker Environmental, Inc., Coraopolis, PA.

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