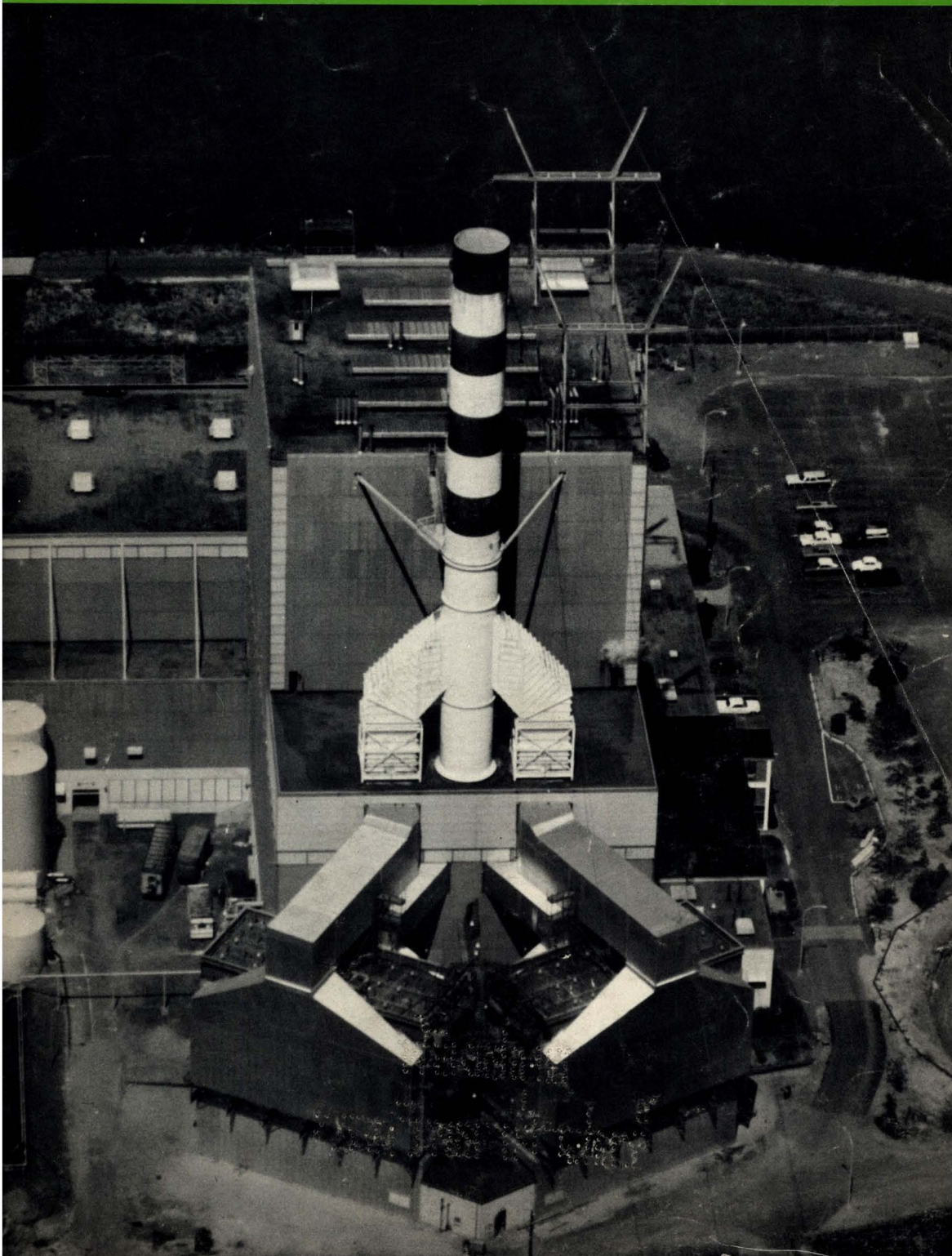
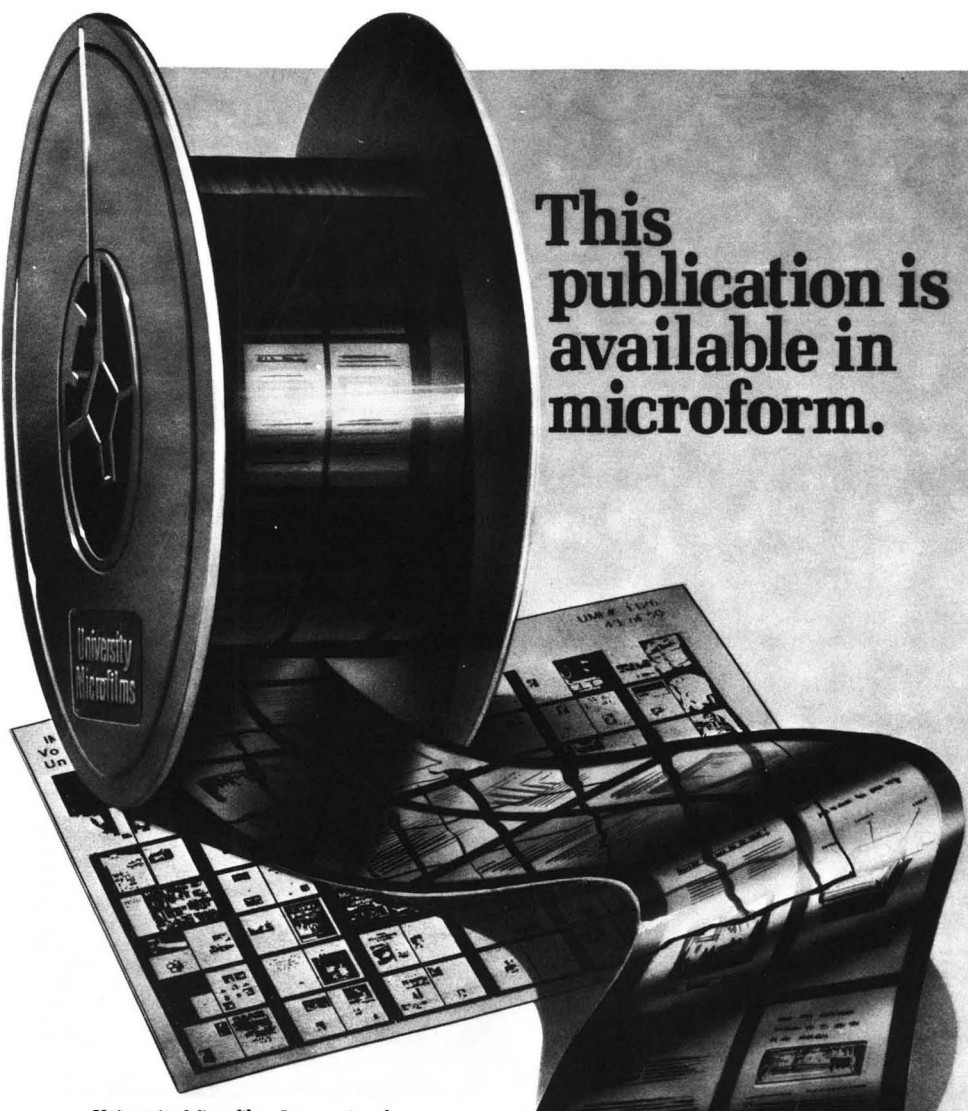


MAY 1988

ENVIRONMENTAL PROGRESS





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Cover: Electrostatic Precipitators similar to the two appearing on the cover are commonly used to remove gas particulates from coal-fire boilers (see article on page 131). Photo Courtesy Research Cottrell Inc., Branchburg, New Jersey.

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A Need for New Consciousness Concerning the Environment

John R. Ehrenfeld

The goal of this Journal can be construed as the reporting of events that have already happened or outlining challenges to be met. One can measure our movement from an old mark in many ways; signs of environmental improvement, new technology deployed, money spent, laws and regulations in place, and so on. Today there would be little debate over any of these issues with respect to the starting line of the 60s and 70s. Increasingly, however, signs of breakdowns in the sequence of events that constitute progress are becoming evident.

As our attention has shifted from earlier, visible signs of environmental degradation to the current focus on more subtle chronic human health effects, it is harder to measure the effects of our actions and inactions. Rather than base our management programs on tangible evidence, we now rely on the indirect evidence of impact on humans. We distinguish a black plume against a clear blue sky or observe the turbidity of our rivers and streams and relate what we find objectionable to particular sources. With carcinogens, our current focus, we cannot easily attribute the illness and deaths we observe to any particular source of these chemicals. Exposure paths exist through all conventional media: air, water, and soil.

Our policy context has become the management of risks. The uncertainty that we attribute to risky situations now pervades all dialogue over environmental issues. The public response to uncertainty tends to be conservative and generally risk-averse. We see resistance to technological approaches to waste management, and increasing demands for waste avoidance and reduction. Siting is at a standstill almost everywhere and our current state is often referred to as gridlock. Broad restrictions on the production and use of chemicals has appeared in California and is on the legislative docket in other states. None of this is necessarily bad but it raises new questions about progress.

It is clear that circumstances have changed and our national policies and efforts in response must change as well. Source reduction is the shibboleth of the present time. Prevention in hazardous substance management, as in medicine, is usually less expensive than the cure. Our views of the sources of the problems must shift from the single media view of the past to a material balance, multi-media framework. Chemical engineers always knew about material balances, but forgot to include the environment within the boundaries for the processes they design.

We need to reexamine responsibilities for planning and building facilities to handle wastes that will continue to be produced while we innovate and learn how to avoid their generation. The top-down technologically-based system of regulations that has been the cornerstone of our policies so far seems ill-equipped to cope with the complexities of our production apparatus. An example is the bureaucratic and technical disaster that the effluent guidelines program has become. New alliances and approaches are needed; the producers of wastes, as well as consumers, need to assume more responsibility for action without waiting for government intervention. Professionals at all levels must get involved.

These approaches are not traditional to our profession and the industry we support. At MIT we have taken an initiative to change that situation; a broad-based hazardous substances management program combining research, education, and policy analysis. The themes are multi-disciplinary, multi-media, material-balance plus participatory and disaggregated decision-making. We aim to instill a new consciousness in all of the professional disciplines that impact the environment, particularly chemical engineering.

Education and research create possibilities of new action in the future. Both are critical to meet current challenges and, in response, we see the growth of commitments at MIT and other academic institutions. But our efforts must be matched by the practitioners already laboring in the fields. As Pogo once said, "We have met the enemy and he is us."

John R. Ehrenfeld is Coordinator, Hazardous Substances Management Program Center for Technology, Policy and Industrial Development at the Massachusetts Institute of Technology, Cambridge, MA 02139.

Commercial Waste Management Firms Predict Reversal in Shortage of Incineration Capacity

EPA Steps Up Waste Site Evaluations in '88

The EPA is scheduled to evaluate 2,000 hazardous waste sites by 1991. Companies named as contributors to these hazardous waste sites will be responsible for the enormous costs involved in cleaning them up.

Companies generating, storing or disposing of hazardous wastes need to be aware of the impending liability brought on by the improper treatment of these hazardous wastes.

To stay abreast with current EPA regulations, companies must consult Title 40 of the Code of Federal Regulations. Parts 100-399 and 700-End of Title 40 are available in four volumes from LabelMaster Division of American Labelmark Co., 5724 Pulaski, Chicago, IL 60646.

The four-volume set includes information for generators of hazardous waste and includes information for owners and operators of hazardous waste treatment, storage and disposal facilities.

For further information call toll-free 1-800-621-5808. In Illinois, call 1-312-478-0900.

Commercial hazardous waste management firms, who in 1985 predicted a severe shortage in commercial hazardous waste incineration capacity, now believe that this deficit does not exist or, if it does, will be short-lived. This was a surprising conclusion of the new ICF Incorporated, Fairfax, VA, survey of 14 major waste management firms, "1986-1987 Survey of Selected Firms in the Commercial Hazardous Waste Management Industry."

According to the survey author Geoffrey Back, who also conducted the 1985 survey, companies in 1985 were nearly unanimous in their view of a chronic lack of commercial hazardous waste incineration capacity. "But in 1987, most of these same firms believe there is no shortage now or that a capacity surplus may exist in the next three to four years as permit applications are finalized," he says. Several factors have contributed to this turnaround in opinion, the survey shows, including a decline in PCP liquids incineration that has freed capacity; the entry of industrial boiler and furnace operators into the waste burning market; efforts to improve the ability of in-

dustrial boilers and furnaces to handle solid and sludge wastes; significant declines in backlogs at some hazardous waste incineration facilities; and the large number of hazardous waste incineration facilities that are in the pipeline to receive permits.

The "wild cards" that will determine the adequacy of future hazardous waste incineration capacity, says Back, include the success of permitting and siting efforts; the timing of land disposal restrictions promulgated by the EPA, particularly regarding CERCLA and RCRA soils and debris; the regulation of industrial boilers and furnaces; and the waste minimization efforts of generators. "Companies thinking about new investments in incineration should wait and see whether additional capacity is needed," he advises. Back expects that profit margins in the hazardous waste market will decline as more companies offer these services.

Copies of the survey are available for \$30.00 each; there is no fee for government organizations. Interested parties should contact Geoffrey Back, ICF Incorporated, (703) 934-3000.

Safe Storage and Handling are Topics of New Guidelines

"The safe storage and handling of high toxic materials (HTMS) require a sound and responsible management philosophy, together with a combination of superior siting, design, fabrication, erection, inspection, monitoring, maintenance, operation, and management of such facilities."

These words appear in the preface of the newest entry in the AIChE's Center for Chemical Process Safety's series of guidelines entitled *Guidelines for Safe Storage and Handling*

of High Toxic Hazard Materials.

The editors go on to say "These elements are necessary parts of a reliable system to prevent equipment or human failures that might lead to the release of, and possible acute exposure, of the public or on-site personnel to HTMS. These Guidelines deal with all these elements including references for mitigating the impact of such releases should they occur."

Overseen by the Center's Storage and Handling Subcommittee, under the leadership of Robert Smith of

Dow Chemical, and prepared by Arthur D. Little Inc., *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* is available from AIChE's Publications Sales Office. Cost to CCPS sponsors is \$40 per copy; AIChE members, \$40 per copy with a one copy limit; non-members \$75 per copy. Foreign orders, please include \$6 postage and handling. Orders should be directed to Publications Sales, AIChE, 345 East 47th Street, New York, N.Y. 10017 or call (212) 705-7657.

Book Reviews

Chemistry for Protection of the Environment: Proceedings of the Fifth International Conference, Leuren, Belgium, September 9-13, 1985. L. Pawlowski, G. Alaerts and W. J. Lacy, editors. Elsevier Science Publishers, 1986. 796 pages, U.S. List price: \$237.

The collection of the conference proceedings was arranged by the editors in a very coherent and consistent manner. The intention of this text is clear, namely the presentation of environmental chemistry problems in a comprehensive way. The chemistry of the environment is not a narrow scientific field, but rather represents an interdisciplinary and multi-media phenomenon. The very title of the book itself is significant in that it is not "environmental chemistry" but rather "chemistry for the environment."

Due to the large number of papers presented at the conference (124 total), the editors selected 59 of the most interesting, valuable, and representative technical papers for this conference proceedings. The titles of several papers were changed slightly from what was listed in the conference program to allow the papers to be grouped according to subject content.

At the beginning of this collection, the opening and closing addresses of Professor Van Haute plus the reflection of Professor W. J. Lacy, co-organizer of the symposium are presented. In his paper "Chemistry for Protection of the Environment, Past, Present, and Future," Professor Lacy discusses the trends of increasing pollutant concentrations and the appearance of new substances as a result of scientific research and its industrial realization. He expresses doubt as to whether legal, technical, and organizational activities undertaken in several developed countries, such as the United States, should be uncritically transferred to other countries.

The first two chapters consist of "Key-Note Lectures" and "General

Problems." Among the eight presentations three deal with the relationship between environmental pollution and public health. In a sense, this relationship is obvious because environmental protection is aimed solely at the protection of mankind from detrimental changes to the environment. Because some technologists, who design and realize investments in the domain of environmental protection, perceive their task in a one-sided way it is necessary to develop a hierarchy of goals. For this reason the paper on "Decision Making in Pollution Control" directly corresponds with this pronouncement. The concept can be reduced to the question of how to best diminish the possible detrimental side effects of the solution alternatives. Other important problems discussed in these chapters include such areas as advanced waste management, the significance of various micropollutants, and heavy metal contamination in a developing tropical city.

Three presentations related to the theme of "Reduction and Oxidative Treatment of Fossil Fuels and Other Chemical Treatments of Waste Streams" appear in the third chapter. Each paper addresses a different phase media: gaseous, liquid and solid. In the latter case, soil and sludges are the focus of attention.

Chapter Four, a group of eight papers on "The Fate of Chemical Pollutants and their Environmental Impact," addresses the analysis of pollutant interaction phenomena on the environment. The details of correlating the physical state and chemical composition of the environment with the emitted pollutants are highlighted, with many examples presented based upon original experimental work. Evaluations of the treatment process performance and the resulting toxicity levels are addressed. Considerable emphasis is devoted to the area of heavy metal contaminants and newly developed organic compounds. At the end of the chapter, a list of substances

being researched or recommended for research by the European Economic Community Commission is presented in the form of an appendix; the reader will find this item to be most valuable.

Only one paper entitled "Physical-Chemical Treatment: Oxidation and Disinfection" appears in Chapter Five. The paper deals with oxidizing photodegradation of organic compounds including several aromatic hydrocarbons and halogen-based derivatives.

Chapters 6, 7 and 8 group papers devoted to physical methods of treatment: flocculation, flotation, filtration and adsorption. Progress in the field and traditional methods of approach are reviewed. A new developing area using membranes for separation is also discussed. One surprising feature to this reviewer is that after the field of ion exchange technology developed very dynamically over the last several years, only three papers were devoted to this subject.

Four papers involving chemical/biological processes in environmental science were grouped in the tenth chapter. Each paper presents a new approach to basic or practical problems not restricted solely to wastewater treatment. The papers also draw attention to chemical/biological methods for waste regeneration or waste utilization.

The next three chapters contain eight papers with the common theme of "Reductive and Oxidative Treatment of Fossil Fuels and Other Organic Chemicals."

The publication concludes with chapter fourteen which addresses "Advances in Environmental Analytical Chemistry." The six papers contained in the chapter deal with the application of the already adopted methods considered vital for the analysis of pollutants, such as ion selective electrodes and gas chromatography techniques. Examples are also given on the application of techniques and chemical determinations for compounds present in trace con-

centrations. An analytical technique applicable to this latter case is atomic absorption.

In conjunction with its title the book provides a wide display of the interactions chemistry provides to the environment. As a result the book places considerable emphasis on the practical, technological, and managerial aspects, including analytical analyses and evaluations. This collection of papers show important trends, aspects, and endeavors underway which are aimed at the protection of the environment through physical/chemical techniques.

Iwo Pollo

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Chemical Quality of Water and the Hydraulic Cycle by Robert C. Averett and Diane M. McKnight, editors. Lewis Publishers Inc., 350 Pages, U.S. List Price \$49.95.

The goal of this book is to present research that emphasizes the

changes that occur in water as it circulates throughout the atmosphere, the earth's surface, and below the earth's surface. The editors have been successful in achieving their aim. Man's activities affect our nation's and world's water supplies. The hydraulic cycle is a complex process involving the complete cycle through which water passes, from the oceans, through the atmosphere, to the land, and back to the ocean. During this process, the various forms of water are circulated throughout the earth's hydrosphere.

The editors of this text have assembled papers which were presented at a symposium entitled "Chemical Quality of Water and the Hydrologic Cycle" at the 8th Rocky Mountain Regional Meeting of the American Chemical Society, held in Denver, Colorado, June 8 through 12, 1986. The text deals with the relationship between hydrologic cycle processes and the chemistry of natural waters. The textbook is divided into four major sections: precipitation chemistry (4 papers); chemistry of ground-water (4 papers); chemistry of surface waters—nutrients,

organic matter, and major constituents (4 papers); and chemistry of surface waters—trace materials (7 papers). Topics such as hydrogeologic aspects of groundwaters and surface anaerobic microbial transformations of azaarenes at hazardous waste sites, roles of anaerobic zones and processes, longitudinal dispersion of trace metals, flood plain storage of metal-contaminated sediments, processes at sediment-water interfaces, adsorption inhibition, and processes affecting vertical distribution in a bog, are discussed.

The papers are appropriate to the areas of chemistry and speciation in natural waters and processes which influence the speciation. This textbook will prove to be a valuable addition and a useful reference source for environmental engineers and scientists, limnologists, hydrogeologists, geologists, and other professionals involved with the chemical quality of water and the hydrologic cycle.

Robert W. Peters

Argonne National Laboratory
Argonne, IL

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Washington Environmental Newsletter

Groundwater Legislation In the environmental area, groundwater quality has become the center of attention in Washington as the EPA released a groundwater protection strategy, and Sen. David Durenberger (R-MN) introduced groundwater legislation in late February.

The EPA plan aims to control pesticide pollution of underground streams and would establish national policies for chemicals known to denigrate groundwater quality. EPA would also specify stricter measures for states and regions where the nature of the soil is conducive to pesticide leaching.

The Durenberger bills (S.2091 and S.2092) would establish a \$900 million annual government program. These bills set a goal of non-degradation of all groundwater and rely *only* on health based standards, regardless of whether or not the groundwater in question is designated for drinking water purposes. A Senate Environment and Public Works groundwater hearing will discuss several pending bills including S.20, S.1105 and H.R. 791 which passed the House late last year.

Prop 65 Becoming Contagious Legislation similar to the controversial California Proposition 65 has recently been introduced in Hawaii and Tennessee. Hawaii's H.B. 2118 requires that no person in the course of doing business shall knowingly and intentionally expose any individual to a chemical known by the state to cause cancer or reproductive toxicity without first giving clear and reasonable warning.

Tennessee's S.B. 1821, the "Safe Drinking Water and Toxic Enforcement Act" requires the Governor to publish a list of chemicals known by the state to cause cancer or reproductive toxicity by March 1, 1989. The bill states that "no person doing business within the state shall knowingly discharge or release any of the listed chemicals into water or onto the land where such chemicals pass or probably would pass into any source of drinking water." This bill is *not* expected to receive serious attention this session.

Waste Minimization EPA has issued letters to states announcing new federal grants for state-run technical assistance programs and waste minimization projects. States will be offered a total of \$3.2 million in grants to set up these projects. For information and a grant application contact Kate Connors, at EPA (202) 475-6647.

Ozone Depletion In addition to the Senate's ratification of the Montreal Protocol on substances that deplete the ozone layer, Sen.'s Chafee, Stafford and Baucus testified that further protection was needed to protect our stratosphere. Sen. John Kerry agreed that more unilateral action was needed and recommended a total 95% phase-out of the CFC and Halon chemical families.

Many manufacturers are opposed to further *unilateral* action that would fail to protect the earth's stratosphere while causing problems for U.S. manufacturers. There is growing support for CRC recapture and recovery and voluntary efforts to substitute substances and processes.

Indications are that Rep. Stark (D-CA) may attempt to include his bill (H.R. 2854) taxing ozone-depleting emissions, in any corrections bill debated in the House Ways and Means Committee.

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

Identification and Quantification of Volatile Organic Species During Microbial Treatment of Leachate

Stephen Sikkema, Erik Dienemann, Robert Ahlert and David Kosson

Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08855

Sequential anaerobic/aerobic microbial populations, in a packed-bed configuration, were employed to biodegrade leachate from a high priority Superfund site. Leachate characteristics included up to 100 ppm (as carbon) volatile organic priority pollutants. Identification and quantification of these pollutants at key steps in the biodegradation process is important. A method employing purge and trap concentration followed by gas chromatographic separation was developed for accurate identification and quantification of the volatile compounds of interest. Results obtained from application of this method to the leachate treatment process indicated that 84 to 99% of the specific volatile priority pollutants were biodegraded, under anaerobic conditions, during steady-state operation.

INTRODUCTION

In January 1985, Rutgers University began a project with the New Jersey Department of Environmental Protection to carry out an "Engineering Analysis of Alternate Treatment for Contaminated Surface Water and Groundwater." The objective of the project was to examine state-of-the-art processes applicable to severely contaminated waters, determine the feasibility of individual processes, and develop overall treatment schemes for contaminated waters. Emphasis was placed on technologies which could be implemented either *in-situ* or on-site. *In-situ* or on-site processes offer both economic and safety advantages by avoiding major excavation and off-site transportation of contaminated wastes.

In September 1985, a high priority Superfund site (an abandoned landfill) was selected for investigation. The major environmental threats associated with the landfill are surface and groundwater contamination resulting from off-site migration of landfill leachate, and secondary air pollution resulting from high concentrations of volatile organic species present in the leachate (see Table 1). Thus, the primary objective of this study was to develop a leachate treatment process to effectively address these threats.

The treatment process selected employs sequential anaerobic/aerobic microbial degradation in packed bed laboratory reactors. This type of process can be easily adapted to *in-situ* or on-site operation. In addition, previous packed column biodegradation experiments have successfully treated a wide variety of wastewaters [1, 2]. Also, these experiments demonstrated that data obtained from laboratory scale experiments are readily extrapolated to field responses. However, the wastewaters treated in these experiments did not contain significant

TABLE I. LEACHATE COMPOSITION

Volatile Organic Species	Concentration (ppb)
Methylene chloride	17,000
Trans 1-2 dichloroethane	570
1-2 dichloroethane	34,000
Trichloroethylene	360
Tetrachloroethylene	73
Benzene	3,800
Toluene	41,000
Total Xylenes	9,400
Ethylbenzene	2,200
Base/Neutral Extractable Species	
Bis(2-chloroethyl)ether	34,000
Bis(2-ethylhexyl)phthalate	760
Dichlorobenzene	310
Diethylphthalate	220
Naphthalene	290
Volatile Fatty Acids	Concentration (ppm)
Acetic Acid	800
Propionic Acid	175
Butyric Acid	125
Isobutyric Acid	100
Other Parameters	
TIC	100
TOC	1,000
VOC	100
TDS	2,000
COD (mg O ₂ /l)	1,700
TKN (mg N/l)	96
Total Phosphorus	<0.2
Sulfate	19
Cyanide	<0.01
Ammonia (mg N/l)	85
Nitrate and Nitrite (mg N/l)	<1.0
Calcium	75.7
Magnesium	11.8
Sodium	81.0
Iron	431

This paper won first place in the 1987 AIChE Environmental Division Student Paper Competition.

levels of volatile organic species. Thus, an important consideration involved in treating the current leachate is the ability to accurately identify and quantify the various volatile organic species present, at all stages of the treatment process. This paper describes the experimental design employed, the development of methods necessary for the analysis of volatile organic species and the important experimental results obtained.

EXPERIMENTAL DESIGN

In January of 1987, an experiment (Exp 0187) was initiated to examine the ability of sequential anaerobic/aerobic microbial populations, in a packed bed configuration, to biodegrade leachate from the high priority Superfund site. In brief summary of Exp 0187, leachate was drawn from collapsible PVC feedbags by a timer-controlled peristaltic pump, and pumped upwards through a 7.6 cm diameter glass laboratory column (LC) packed with a sandy loam soil. PVC bags were used as they exhibit the lowest gas permeability of commercially available polymer sheets. This column was maintained under anoxic conditions to promote anaerobic microbial degradation of the organic constituents present in the leachate. This was intended to encourage degradation of the most volatile organic species (chlorinated, short-chained alkanes) first; it has been shown that these compounds are most effectively biodegraded anaerobically [3, 4].

Liquid effluent from this column passed directly into, and upwards through, a second 7.6 cm diameter glass column. The second column was packed with coarse sand and intermittently fed oxygen gas to promote aerobic microbial degradation of organic constituents remaining after anaerobic treatment. Both columns were 122 cm high. The aerobic and anaerobic columns employed identical gas collection systems to allow for identification and quantification of gases produced during biodegradation. The design allowed for addition of nutrient solution at the bottom of each column, and syringe sampling of the liquid effluent at the top of each column (see Figure 1). The entire experimental apparatus was kept airtight to prevent contamination due to atmospheric infiltration, and losses due to volatilization of organic species. Experiment 0187 employed two sequential anaerobic/aerobic bioreactors as replicates (LC 5 soil/sand and LC 6 soil/sand). A similar experimental design was used in a previous experiment with the same leachate and is described fully by Dienemann, *et al.* [5].

Experiment 0187 operated at steady-state conditions from May through September 1987. During steady-state operation, the anaerobic column removed approximately 80% of the total organic carbon (TOC) present in the influent leachate (leachate TOC is approximately 1000 ppm), while the aerobic column removed approximately 55% of the TOC remaining after anaerobic treatment; thus, the overall TOC removal rate was in excess of 90%. These TOC values do not include the volatile organic species that comprise approximately 10% of the influent organic carbon and were the primary focus of the study.

ANALYTICAL APPROACH/METHODS DEVELOPMENT

A sample of leachate taken from the contaminated site was subjected to a full priority pollutant analysis by a commercial laboratory. Results from that analysis and other analyses performed at Rutgers are summarized in Table 1. The priority pollutants benzene, toluene, 1,2 dichloroethane (DCE), methylene chloride (MECL) and ethyl-benzene (ET-BENZ) account for over 90% of the volatile organic fraction of the leachate. Development of a method to assay these compounds, in a complex matrix

and over a wide range of concentrations, was necessary.

The literature advised that a purge and trap concentrator, in series with a gas chromatograph (GC) containing a wide bore (0.750 mm ID) capillary column and a flame ionization detector (FID), would provide the sensitivity and resolution necessary for routine identification and quantification of the volatile organic species [6].

Purge and trap concentration employs inert gas (He) stripping of volatile species from liquid (generally aqueous) samples. Compounds entrained in the purge gas are adsorbed onto a tenax trap maintained at room temperature. The trap is heated ballistically to a temperature well above the boiling points of all adsorbed species; species are desorbed from the trap and swept into the gas chromatograph by the carrier gas. Detection sensitivities are increased 5000 times relative to direct injection of sample. The purge and trap concentrator used was a Chemical Data Systems Model 320. The gas chromatograph used was a Hewlett-Packard 5880A, and the column was a Supelco VOCOL, 60 m \times 0.75 mm ID, 1.5 μ m film.

The detector used for this investigation was a Hewlett-Packard flame ionization detector (FID). The detection signal is roughly proportional to the number of carbon atoms in the molecule. Thus, the FID is more sensitive to non-halogenated compounds, as an example. FID response is generally linear over the range of 50-1000 ng carbon.

The following external standard method was used to establish concentration ranges and standard curves for the volatile compounds in the leachate. A pure stock, standard solution of each compound in a methanol matrix was prepared, at approximately 1000 ppm. Methanol was used to obtain optimum solubilities and minimize volatilization losses. Gravimetric and volumetric methods were tested for preparation of standard solutions. Solute volatility losses and solvent evaporation losses severely limited the precision of gravimetric preparations of standard solutions. When analyses using accurate gravimetric standards were compared with those obtained using volumetric standards, the percent error was negligible. Since volumetric preparation was also much easier, it was chosen over gravimetric preparation.

A known mass (volume, usually less than 5 μ l) of solute was taken from stock solution and diluted in 5 ml of deionized water and immediately injected into the purge and trap unit for analysis. A range of masses for each compound of interest produced peak area responses from the detector. Masses, accounting for solvent density differences, were then plotted versus area responses to develop standard curves for compounds of interest. Standard curves were regressed linearly to standard curve equations with which to calculate concentrations of compounds in actual process samples. For process samples of "unknown" composition and concentration, retention times and spike addition were used to identify compounds of interest. Process samples included influent leachate, effluent from the anaerobic column and effluent from the aerobic column. Once identified, peak area responses were used in conjunction with the standard curves to calculate species concentrations for process samples.

Before purge and trap/GC could be used fully as an analytical method, minimal system losses had to be demonstrated and operational parameters had to be optimized. Equal masses (volumes) of standard solutions were analyzed by direct injection into the GC and by aqueous dilution followed by purge and trap/GC, to determine sample losses. Theoretically, the area responses obtained using purge and trap should be identical, for the same mass of species introduced, as for direct injection, if there are no losses. In reality, there is always some loss (volatil-

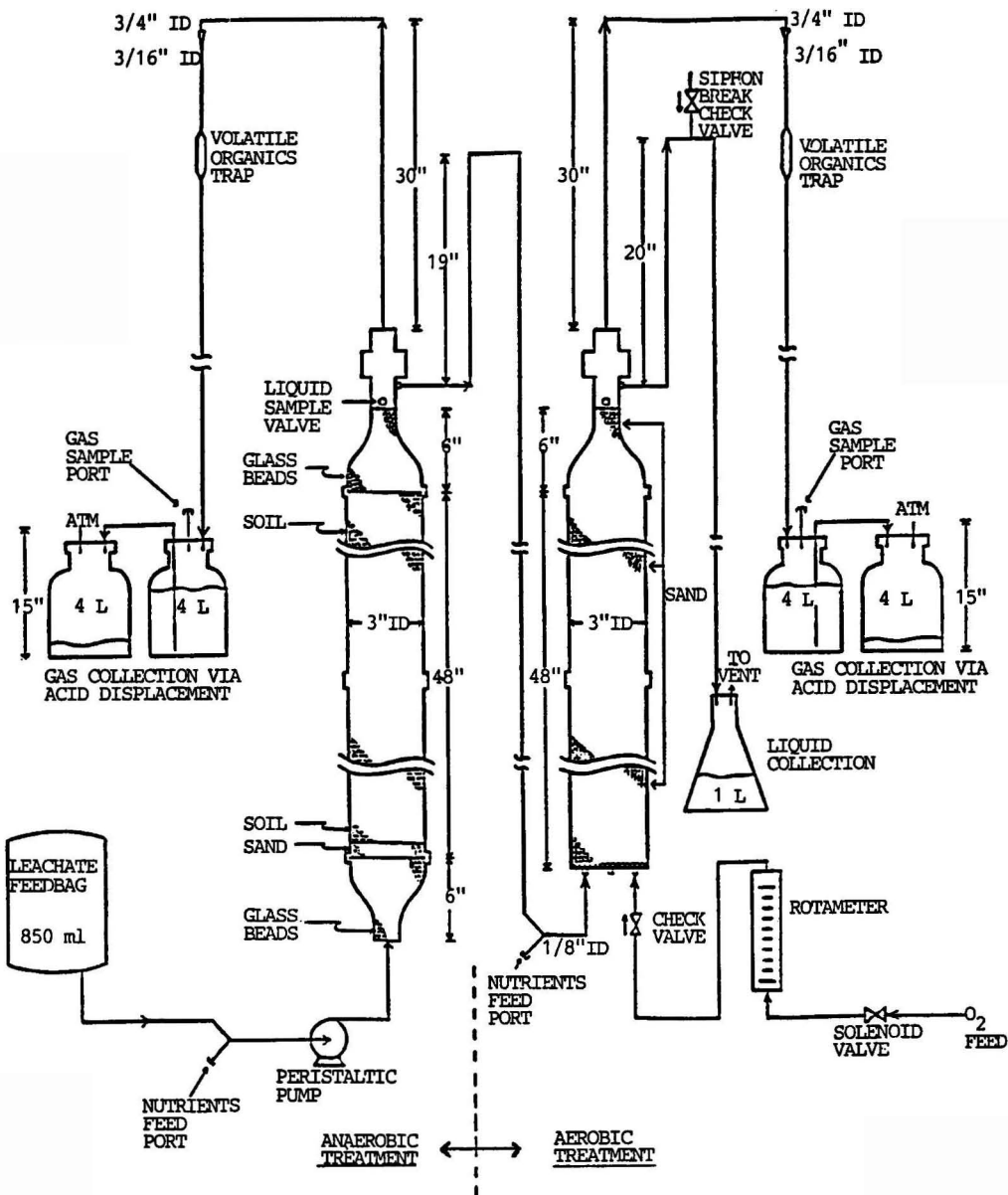


Figure 1. Schematic diagram of sequential anaerobic/aerobic packed bed bioreactor.

ization losses from syringe or sparge vessel, incomplete trapping of species, etc.), but in this study these losses were less than 10%. This indicated that the purge and trap procedure could be used with confidence on unknown aqueous samples.

Optimization was a two-stage process involving optimization of purge and trap parameters and optimization of gas chromatographic parameters. Samples of leachate were used for method development as they were likely to be the most difficult samples. For the purge and trap, it was found that a sparge time of 15 minutes with a sample volume of 5 ml resulted in maximum recovery of volatile

species. A trap desorption temperature of 250°C was necessary to fully desorb all organic species. For the GC, a multi-level oven temperature program was necessary to effect adequate separation and resolution of all species. Optimal purge and trap and GC parameters are presented in Table 2. The same purge and trap and GC parameters were employed for analysis of all standards and process samples.

Spike addition was employed occasionally as a verification tool for components of interest present in process samples. A known amount of pure standard (or mixed standards) was injected into a sample that has been ana-

TABLE 2. GAS CHROMATOGRAPH PARAMETERS

Oven Temperature Profile:

Initial Value = 35°C

Initial Time = 8 minutes

Level 1

Program Rate = 4°C/min

Final Value = 50°C

Final Time = 0.1 min

Level 2

Program Rate = 10°C/min

Final Value = 250°C

Final Time = 20 minutes

Injector Temperature = 250°C

Detector Temperature = 250°C

Chart Speed = 1.27 cm/min

Attenuation = 2.5

Percent Offset = 10

Threshold = 4

Peak Width = 0.16

Purge and Trap Concentrator Program

Function	Temperature (C)	Time (min)
Sparge	Ambient	15
Dry Trap	35	5
Desorb Trap	250	5
Bake Trap	250	5
Valve Oven	250	Continuous
Transfer Line	250	Continuous

lyzed previously. The area response at a specific compound retention time increases relative to the amount of pure compound added to the sample. This permits the identification of compounds present in process samples with a high degree of confidence.

RESULTS AND DISCUSSION

Quantification of Influent and Effluent

The analytical methods discussed above were applied to influent leachate samples and effluent samples from both anaerobic and aerobic columns, in order to identify and quantify the volatile compounds of interest. Effluent samples were taken from the syringe sampling valves on the anaerobic/aerobic columns. All samples were filtered through a 0.45 micron syringe filter and stored in 2 ml vials, without headspace, at 4°C. Samples were analyzed within two days.

If necessary, process samples were diluted with deionized water, immediately before analysis, so that volatile

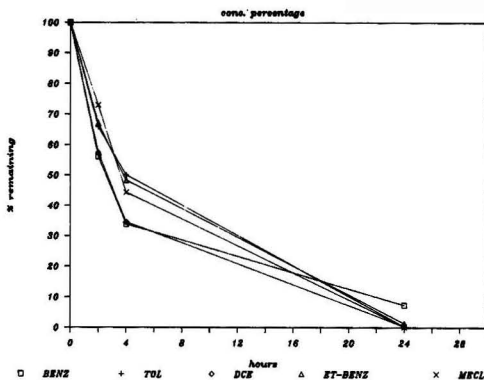


Figure 3. Free volatilization rate.

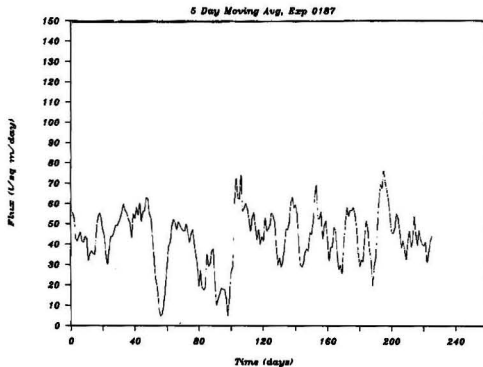


Figure 4. Hydraulic flux, LC 6.

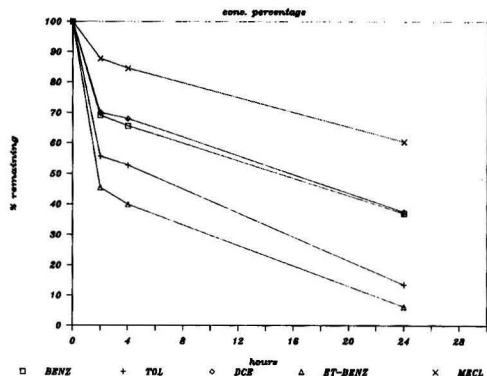


Figure 2. PVC bag volatilization rate.

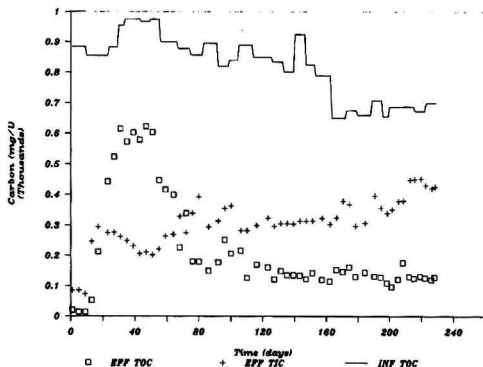


Figure 5. LC 6—anaerobic column.

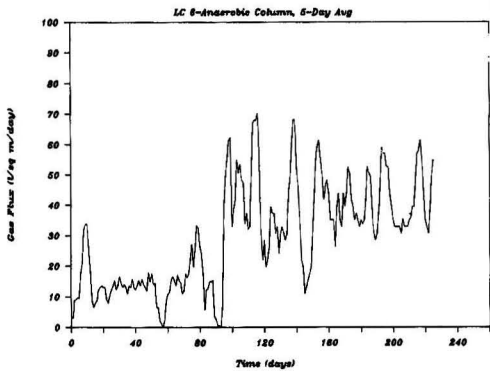


Figure 6. Effluent gas flux, exp 0187.

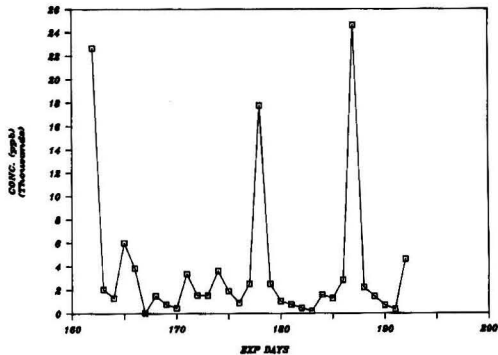


Figure 9. Volatile influent conc.—toluene.

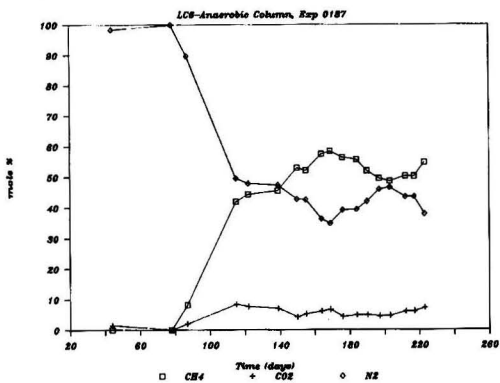


Figure 7. Effluent gas composition.

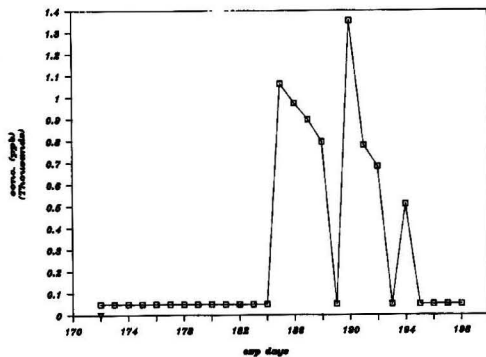


Figure 10. Volatile effluent conc.—methylene chloride.

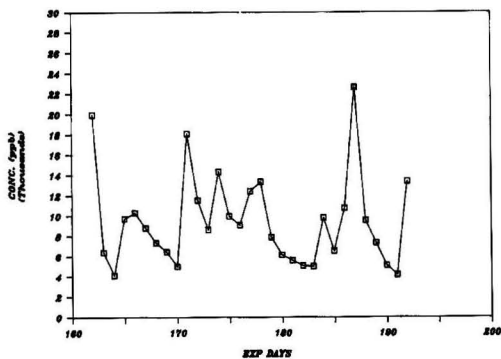


Figure 8. Volatile influent conc.—methylene chloride.

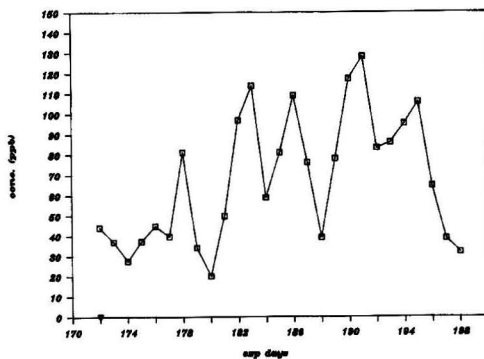


Figure 11. Volatile effluent conc.—toluene.

organic species responses were within the range of the external standard curves generated for the compounds. All analyses (standards and process samples) were performed in duplicate, at least, and often in triplicate. Reproducibility was general excellent; the standard deviation was less than 5% of the mean.

Analyses successfully identified and quantified the five volatile organic compounds of interest in the leachate, i.e., benzene, toluene, methylene chloride, ethylbenzene and 1,2-dichloroethane. The results of influent leachate analyses compare favorably to the results reported by the commercial laboratory (see Table 1). Differences were probably due to differences in sample containment, biodegradation before analysis, volatilization losses from sample containment transfer, and the different analytical methods employed.

Anaerobic effluent contained two compounds of interest above detection limits (50 ppb) and three unknown species of greater concentration. Aerobic effluent did not contain any of the known volatile species above detection limits; it did contain the same three unknown species, as were in the anaerobic effluent, but in lesser concentrations.

Volatilization Losses from PVC Feedbags

Collapsible PVC feedbags were employed to supply the columns with leachate; the leachate was refrigerated in 4-liter amber bottles, without headspace, prior to use as column influent. Initially, it was assumed that volatilization losses through the feedbags was minimal during the period in which a bag was being used (about four days of feeding per bag at an average flow rate of 250 ml leachate/day). An experiment was performed to test this assumption. Samples were taken from a feedbag when it was initially filled ($t = 0$) and in an hourly geometric progression ($t = 1, 2, 4, \dots$ hrs). Samples were also taken at the same times from an open beaker containing the same leachate, to measure the rate of free volatilization of the compounds of interest.

Data are presented as percent remaining versus time for the five compounds of interest, for volatilization from the PVC bag (Figure 2) and free volatilization (Figure 3). The data show that over 50% of these compounds (except MECL) are lost from the bag in 24 hours; almost 100% of these compounds are lost from an open container in 24 hours. The more volatile (as pure components) compounds, MECL and DCE, display the slowest bag volatilization rate. This is most likely due to a combination of greater water solubility and less ability to permeate the PVC polymer due to the presence of chlorine atoms. The loss of these compounds from the feedbags complicated attempts to calculate treatment process mass balances for these species.

Volatile Species Mass Balances

Mass balances were calculated for the five volatile compounds of interest, over a 26 day period of steady-state column operation, for the anaerobic stage of LC 6. Steady-state conditions were defined by limited fluctuations in effluent total organic carbon (TOC) concentration and effluent total inorganic carbon (TIC) concentration, hydraulic flux rate, and gas production rate and composition; see Figures 4 to 7. Samples of leachate influent were taken daily from Day 162 to Day 188, while anaerobic and aerobic effluent samples were taken from Day 172 to Day 198. All samples were taken in 2 ml vials, without headspace, and analyzed within two days. Samples were taken every day in anticipation of significant daily fluctuations of volatile compound concentrations, due to volatility losses. It was thought that daily sampling would be nec-

essary to define these fluctuations adequately, especially when feedbags were refilled with fresh leachate.

Influent volatile organic concentrations are compiled for the 26 day period, for two of the compounds of interest, MECL and toluene, in Figures 8 and 9, respectively. There were significant influent concentration fluctuations for all of the compounds. The large concentration peaks generally corresponded to the use of freshly refilled feedbags; influent concentrations then fell rapidly, as seen in the feedbag volatilization experiment. Influent volatile organic species concentrations did not become negligible, however, especially for the chlorinated compounds. The anaerobic effluent contained two compounds, methylene chloride and toluene, which were periodically above minimum detection limits (50 ppb). These data are presented in Figures 10 and 11. The concentration of these compounds in the anaerobic effluent was much lower than in the influent, however; there was no clear relationship between influent and effluent fluctuations. The aerobic effluent did not contain any of the compounds of interest at any time; it is quite possible that any remaining volatile species entering the aerobic column were stripped out of solution by the intermittent oxygen flow.

Daily influent/effluent volatile compound masses (μg) were computed by multiplying the daily influent/effluent compound concentration ($\mu\text{g/L}$), calculated by external standard methods, and the daily column volumetric throughput (L). These daily masses were then summed over the 26 day period to obtain overall influent and effluent volatile compound masses. There is a 10 day offset in calculation of the overall influent and effluent masses, to compensate for the hydraulic residence time in the anaerobic column; for example, a major influent concentration fluctuation on Day 4 would most likely be reflected in the effluent on Day 14.

The overall leachate influent masses, overall anaerobic effluent masses and mass removal percentages are compiled for each compound of interest in Table 3. These data point to between 84 and 99% removal during steady-state operation. It can be estimated that most of this removal was due to anaerobic microbial degradation. Other possible removal phenomena are unlikely. By Day 160, all of the adsorptive capacity of the column packing should have been exhausted several times over, and further volatilization losses were unlikely, given the airtightness of the system. In addition, the reduction in TOC and production of common anaerobic respiration and fermentation gases are further evidence of a thriving mixed anaerobic community.

CONCLUSIONS

An analytical methodology employing purge and trap concentration followed by capillary column gas chroma-

TABLE 3. STEADY STATE VOLATILE SPECIES MASS BALANCES* FOR THE ANAEROBIC COLUMN LC 6-SOIL

Compound Of Interest	Influent Mass (μg)	Effluent Mass (μg)	Removal Percent
Benzene	1964	310**	84
Toluene	17980	431	98
1,2 Dichloroethane	41180	310**	99
Ethylbenzene	3181	310**	90
Methylene Chloride	114100	1592	97

*Balances were compiled over a 26 day period during steady state operation.

**These compounds were never detected above the minimum detection limit of 50 $\mu\text{g/l}$; sample concentrations were assumed to be 50 $\mu\text{g/l}$ in these cases.

tographic separation with FID detection was developed for accurate identification and quantification of volatile organic species. These species are present as a complex mixture in leachate from a high priority Superfund site. Application of this methodology to an experimental microbial leachate treatment process indicated that between 84 and 99% of the specific volatile organic species were biodegraded under anaerobic conditions, during steady-state operation.

ACKNOWLEDGMENTS

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The Simultaneous Removal of Oil and Heavy Metals From Industrial Wastewater by Joint Precipitation and Air Flotation

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A joint precipitation and air flotation system was used to simultaneously remove oil and heavy metals from an industrial wastewater. The wastewaters were subjected to hydroxide treatment and chemical collectors simultaneously. The flotation tests were run for 4 min. For the particular wastewaters studied, the optimal pH and air injection rate was 9.18 and 12,150 cm³/min, respectively. Three different chemical collectors were investigated (WOF-67, Nalco-7182, and Jayfloc-806); the optimal collector dosage was typically in the range of 2-5 mg/L (depending on the particular chemical collector and heavy metal of concern). Removals of the heavy metals and oil typically exceeded 85%; oil removals are great as 96.2% were achieved. Removal of the heavy metals and oil probably occurred through a coprecipitation-adsorption mechanism. Removals of the various heavy metals compared favorably between the individual removal and simultaneous removal (of heavy metals and oil) studies. By appropriate choice of the chemical collector, its dosage, pH and air injection rate, the selectivity for individual metal species can be affected.*

INTRODUCTION

The sources of heavy metals in industrial wastewaters are diverse and include the steel and metal finishing, plating baths, handling of metal containing petroleum-based compounds, and battery manufacturing. Oils are commonly associated with the metals; these oils may be suspended, emulsified, or dissolved. Oil concentrations greater than 1,000 mg/L are not uncommon in industrial wastewaters [5].

Limiting metals and oils in industrial effluents is im-

portant whether these effluents are discharged either directly to waterways or to publicly owned treatment works. Because of the continued degradation of the waters of the nation, both by industries and municipalities, the government responded with the Clean Water Act of 1972 (Pub. L. 92-500), Section 307 of which clearly states that the levels of heavy metals, oils, and cyanides should be reduced to acceptable levels even in wastewater discharges to sewers.

To date, heavy metals and oils have been removed from wastewaters separately and by completely different treatment processes. The usual method of oil removal has been simple American Petroleum Institute (API) gravity separation, possibly followed by air flotation. Heavy metals are normally removed by precipitation and sedimentation, typically with hydroxide treating agents but in some cases with sulfides, borohydrides, or starch xan-

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*References in this paper to commercial products do not constitute or imply an endorsement of these products by the authors.

thates.

The solubility of all metals in water is a strong function of pH. To remove metals from wastewaters, the pH is adjusted until the metals exhibit their minimum solubilities. However, the pH for minimum solubility is different for each metal. Thus, to treat a wastewater containing several heavy metals, an optimal, though compromise, pH has to be chosen to attain satisfactory removal of all metals but possibly not the maximum removal for any one, as illustrated in Figure 1.

Since API gravity separation does not remove emulsified oils from wastewaters, air flotation is often used to remove such oils, especially when the emulsion is broken chemically.

BACKGROUND

The conventional method for precipitating metals is by addition of hydroxide. A more efficient method involves sulfide precipitation. Odor problems resulting from hydrogen sulfide formation have generally restricted the use of this technique. Recent research, however, has indicated that this problem can be controlled through understoichiometric addition of sulfide, resulting in a coprecipitation-adsorption mechanism for heavy metal removal [4, 12, 13]. Hydroxide addition to precipitate the metals is relatively safe, although the amphoterism of metal hydroxides creates difficulties through resolubilization [14].

Almost all oil in the suspended-free form is removed by API gravity separation. To remove oil in the dissolved or emulsified forms, air flotation (dissolved and induced) is used extensively, especially following chemical addition to break the emulsion.

In the hydroxide precipitation process, heavy metals are removed by adding an alkali such as caustic, lime, or soda ash to adjust the wastewater pH to the point of minimum metal solubility. The extent of precipitation depends on the solubility product (K_{sp}) of the metal hydroxide, which is quite low. Since the precipitates formed are insoluble, the residual metal concentrations in solution are quite low. The extent of precipitation also depends on several parameters, such as pH, type of metal in solution, and presence of other ions in solution [3]. The effect of various complexing agents on precipitation of cadmium and zinc hydroxides has been studied by Ku and Peters [9]. The precipitates are generally amorphous in nature, hindering solid-liquid separation procedures [11].

Air Flotation Systems

By applying the principles of buoyancy, air flotation processes use air bubbles to lift a second phase in a liquid to the surface. The rise rate of the air bubbles is governed by Stokes' equation, which applies when the bubbles and their attached solids are sufficiently small that creeping flow occurs. The greater the contact angle between the particle surface and the bubble, the greater the floatability of a particle. The factor that determines a particle's contact angle with water, and hence its floatability, is the hydrophobicity. Particles are either hydrophobic or hydrophilic. Certain compounds called collectors are organic molecules or ions that selectively adsorb onto particle surfaces. Collectors are weak acids, bases, or their salts, and are heteropolar with two functional ends: ionic and organic. The ionic group adsorbs to the particle surfaces. The organic group provides the hydrophobic surfaces to the particle.

The principal components of a dissolved air flotation (DAF) system are a pressurizing pump, air supply, retention tank, and flotation unit. The system can be operated with or without recycling. Operating variables include air pressure, recycle ratio, detention time, air/solids ratio, solids and hydraulic loading rates, and application of chemical aids. Operating air pressure in the dissolution tank influences the size of bubbles released. If the bubbles are too large, they do not attach readily to the sludge particles, whereas too small a dispersion causes the fragile flocs to shatter. Generally, bubble sizes less than 100 μm are desirable. To establish the proper rise rate, experiments must be performed at various air pressures.

Induced air flotation processes use bubbles generated by high-speed rotating impellers, diffusers, or nozzles. These kinds of equipment usually generate bubbles in the range of 400-2,000 μm . These processes offer several advantages over the DAF systems: reduced residence times (and hence reduced equipment sizes) and reduced costs. In addition, they eliminate the pressurizer/saturator of the DAF systems.

Nozzle air flotation processes use a gas aspiration nozzle that draws air into the wastewater to form a two-phase mixture of water and air. The mixture is turbulent and well mixed as it enters the flotation cell.

Previous Related Research

Mukai *et al.* [10] studied the removal of metal ions by coprecipitating them with ferric hydroxide and subsequently eliminating the coprecipitate by flotation. Favorable pH ranges were found for each metal hydroxide: pH 8.5-9.2 for zinc (Zn), pH 8.5-10.1 for copper (Cu), and pH 8.5-11.6 for cadmium (Cd). However, little research has performed on the simultaneous removal of oil and metals.

Ching [6] studied the simultaneous removal of heavy metals and oil by DAF. This study was particularly important because most researchers agreed that both processes occurred simultaneously, but few workers had measured them in a treatment study. Ching's work was limited to a bench-scale DAF simulation. The wastewater was synthetically prepared using mixtures of cupric acetate, zinc sulfate, lead acetate, and oil in deionized distilled water. The tests were conducted in a batch mode, and the experimental variables were the collector dosages, pH, applied pressure, and percent recycle.

The Ching study used three precipitants (lime, sodium sulfide, and sodium carbonate) and four chemical collectors (sodium lauryl sulfate, Nalco 7734, Atlasep 2A2, and Tretolite TFL-365). For the synthetic wastewater used, 86.5 mg/L Atlasep 2A2, 144.2 mg/L Nalco 7734, and 86.5 mg/L sodium lauryl sulfate resulted in the minimum residual metal concentrations when employing the pre-

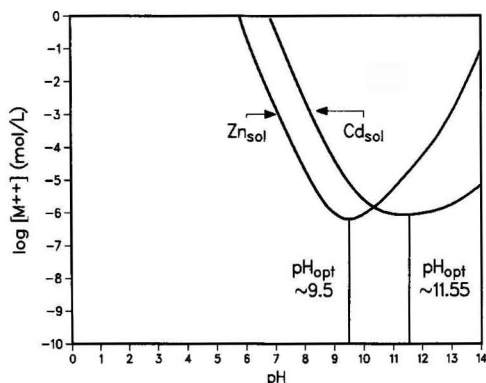


Figure 1. Logarithmic plot of the soluble metal concentration as a function of pH for the $\text{Zn}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ systems.

precipitants calcium hydroxide, sodium sulfide, and sodium carbonate, respectively. Values for other parameters determined as optimal were a pH of 8.5, an applied pressure of 45 psig, and 30% recycle. For an industrial wastewater from a barrel drum plant, calcium hydroxide and Tretolite-365 proved to be the optimal precipitant and collector, respectively. Analysis of the treated wastewater showed residual concentrations of 0.66 mg/L lead (Pb) (76% removal), less than 0.19 mg/L Cu (98% removal), 1.81 mg/L Zn (50% removal), and 350 mg/L oil (91% removal). Results confirmed the hypothesis that simultaneous removal of metals and oils were indeed possible by flotation with oil removals in excess of 90% being achieved and heavy metals removals being in excess of 70%.

RESEARCH OBJECTIVES

This research project focused on a joint precipitation and air flotation process to simultaneously remove oil and heavy metals (Zn, Cu, and Pb) from industrial wastewaters. The objectives of this research are summarized below:

1. To determine the feasibility and applicability of this innovative precipitation-flotation process by performing a series of jar tests in the laboratory.
2. To conduct a series of jar tests to determine optimal pH for heavy metal removal in the flotation trials.
3. To determine adequate chemical collectors by screening various collectors, including Nalco-7182, WOF-67, and Jayfloc-806.
4. To investigate the effects of collectors and dosages on the simultaneous removal of oil and heavy metals performed at the optimal pH.
5. To investigate the effect of air injection rate on the residual metal concentration and investigate the performance of two types of air flotation systems (induced and nozzle air flotation).

To our knowledge, few such studies have been performed previously to address the simultaneous removal of oil and heavy metals from industrial wastewaters. This research addresses that void in the technical literature.

EXPERIMENTAL EQUIPMENT

To evaluate the removal of dissolved heavy metals and oil from industrial wastewaters, two different air flotation units were used: an induced air flotation unit and a nozzle air flotation unit, both built by Wemco Corp. An atomic absorption spectrophotometer (Perkin-Elmer Model 3030) were used to determine the soluble metal concen-

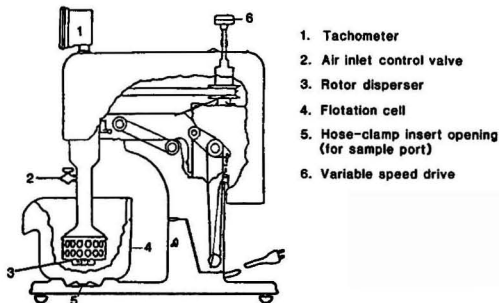


Figure 2. Schematic diagram of the impeller-type induced air flotation machine (Wemco Corp., Sacramento, Calif.).

trations, while Freon extraction was used to determine the oil concentrations. The two air flotation units are described below.

Induced Air Flotation Unit

For the induced air flotation trials, a laboratory model manufactured by Wemco was used. The air flotation cell (Fagergren model) used is illustrated in Figure 2. The cell consists essentially of a batch flotation unit and includes a tachometer to indicate the speed of the machine's rotor, an air inlet control valve to regulate the quantity of air being drawn into the cell by the rotor, and an adjustable, multiribbed rotor disperser to control surface turbulence during the flotation runs. A 3.0-L glass, open-top flotation cell with a drain plug at the bottom (to allow for removal of samples for analysis) was used during the flotation trials. An overflow weir at the upper rim of the flotation cell allows for removal of wastewater or the froth generated during the experimental run. The unit containing 2.5 L of wastewater was operated at rotor speed in the range of 850-1,500 rpm.

Nozzle Air Flotation Unit

The nozzle unit in air flotation systems is a recent development. The injection device uses a gas aspiration nozzle (an eductor-exhauster), shown schematically in Figure 3, to draw air into recycled treated wastewater and develop a two-phase mixture of air and water. That mix-

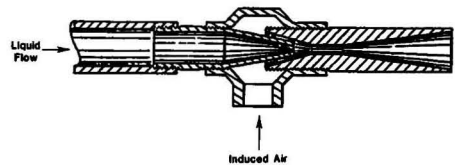


Figure 3. Aspiration of air into a fluid at the throat of a venturi (Source: Bennett 1986).

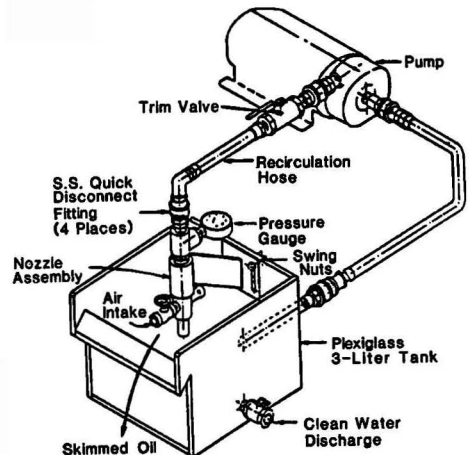


Figure 4. Schematic diagram of the single-stage nozzle air flotation system (Wemco Corp., Sacramento, Calif.).

ture is discharged into the flotation cell. The fluid flowing into the venturi causes a vacuum at the throat. The nozzle air flotation system is shown in Figure 4. Advantages claimed for the nozzle unit over conventional induced air flotation systems include:

- Lower initial cost and energy usage because a single pump provides the mixing and air supply.
- Lower maintenance and longer life because the unit has no high-speed moving parts to wear out.

EXPERIMENTAL PROCEDURE

The primary aim of the preliminary jar tests was to determine an optimal pH for the subsequent flotation trials. The pH at which metals exhibit minimum solubilities is different for each metal. Hence, a compromise "optimal" value of the pH had to be selected. With this objective in mind, a series of jar tests were performed. A standard solution of Zn, Cu, and Pb was prepared from Atomic-Absorption-grade zinc sulfate, cupric acetate, and lead acetate. The pH was adjusted with reagent-grade sodium hydroxide solution. The temperature during these jar test experiments and the flotation experiments was held constant at $25.0 \pm 2.0^\circ\text{C}$.

Following the jar tests, the experimental moved to the flotation tests. Known volumes of the industrial wastewaters containing oil and heavy metals were placed in the flotation units. After pH adjustment with hydroxide to reach the optimal pH (selected on the basis of the jar tests), a known amount of the polyelectrolyte (collector) was added, and the flotation tests were run for 4 min. Samples were drawn off the bottom of the unit and filtered through a $0.45\text{-}\mu\text{m}$ filter; the filtrate was analyzed for residual concentrations of Zn, Cu, and Pb. The variables used in these tests include the dosage of the collectors, type of collector, and type of wastewater. The metal concentrations were determined using a Perkin-Elmer Model 3030 atomic absorption spectrophotometer. The wastewaters used in these tests were obtained from industries near Toledo, Ohio.

Three different chemical collectors were employed in this study. The collector WOF-67 from Western Chemical Company is an anionic flocculant that has proved effective in many solid-liquid separation processes. It is a liquid emulsion of high molecular weight with polyacrylamide as its structural type. Jayfloc-806 from Exxon Chemicals is a high-molecular-weight (about $8\text{-}10 \times 10^6$), medium-charge-density, anionic emulsion polymer. Nalco-7182 from Nalco Corp. is a high-molecular-weight anionic collector. All three collectors have proved effective over a wide pH range.

RESULTS AND DISCUSSION

Preliminary Results from the Jar Tests

Table 1 summarizes the obtained residual concentrations of Zn, Cu, and Pb as a function of pH using WOF-67 (the results are shown in Figure 5). The metals typically exhibited their minimum residual concentration for pH in the range of 8.5-10.5 (for metal hydroxide precipitation). The optimal operating pH was determined to be about 9.18 on the basis of the jar test results. The optimal pH may differ from other wastewaters, collectors, and air flotation systems.

The residual metal concentrations obtained from the jar tests were likewise plotted as a function of pH in Figure 6; also plotted in Figure 6 are the theoretical solubilities of various metal hydroxides and metal sulfides (obtained by considering the metal mass balances, solubility products, and metal hydroxyl complexes). Of particular interest to this study are the curves for zinc hydroxide, $\text{Zn}(\text{OH})_2$; copper hydroxide, $\text{Cu}(\text{OH})_2$; and lead hydroxide, $\text{Pb}(\text{OH})_2$. The metals Zn, Cu, and Pb were present in the wastewaters used in this study. Several interesting features are seen in Figure 6. The residual Zn concentra-

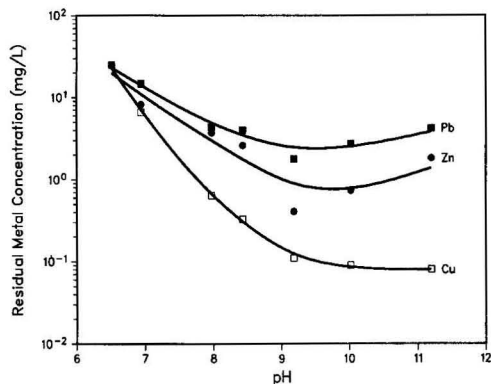


Figure 5. Residual metal concentration obtained from jar tests as a function of pH.

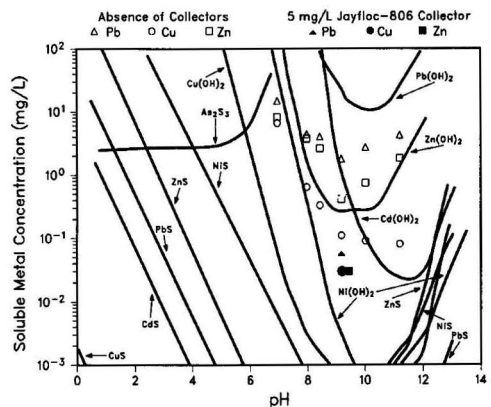


Figure 6. Comparison of experimental residual metal concentrations obtained with the predicted residual metal solubility (based upon mass balance, solubility product, and metal hydroxyl complex formation) as a function of pH.

TABLE 1. RESIDUAL METAL CONCENTRATIONS AS A FUNCTION OF pH FOR WOF-67 IN THE BATCH METAL HYDROXIDE PRECIPITATIONS^a

Sample pH	Residual Metal Concentration (mg/L)		
	Zn	Cu	Pb
6.51	25.00	25.00	25.00
6.94	8.19	6.56	14.72
7.97	3.72	0.64	4.36
8.43	2.61	0.33	3.99
9.18	0.41	0.11	1.78
10.02	0.74	0.09	2.72
11.20	1.82	0.08	4.21

^a Initial wastewater composition: $\text{Zn}_i = 25.0 \text{ mg/L}$, $\text{Cu}_i = 25.0 \text{ mg/L}$, and $\text{Pb}_i = 25.0 \text{ mg/L}$.

tions conform reasonably well with the predicted solubility for $Zn(OH)_2$. The results for Cu do not seem to be in good agreement with that predicted for $Cu(OH)_2$ precipitation; the observed residual Cu concentration is about two orders of magnitude greater than the predicted solubility. This disagreement may be due in part to the sample concentration being near the limits of detection; no concentrating techniques were employed to check the accuracy of the concentrations obtained. The residual Pb concentrations are nearly one to two orders of magnitude lower than the predicted solubility for Pb, assuming $Pb(OH)_2$ precipitation occurs. Lead hydroxycarbonate, $Pb_3(OH)_2(CO_3)_2$, was determined not to be the predominant lead-containing precipitate form. The behavior for these three metals suggests that a coprecipitation-adsorption behavior is occurring. The solubility products for $Zn(OH)_2$, $Cu(OH)_2$, and $Pb(OH)_2$ are $10^{-16.7}$, $10^{-20.4}$, and $10^{-15.3}$ mol³/L³, respectively [1,7]. Lead is the most soluble of the three metals studied, while Cu is the least soluble. Copper hydroxide likely serves as seed for $Pb(OH)_2$ precipitation by providing sites for precipitation. The soluble Pb and Zn may adsorb onto the $Cu(OH)_2$ amorphous precipitates formed. The adsorption of Pb and Zn blocks sites for $Cu(OH)_2$ precipitation, thereby hindering $Cu(OH)_2$ growth and nucleation rates.

Figure 6 also shows the residual metal concentrations obtained with Jayfloc-806 applied at a dosage of 5 mg/L; considerably lower residual metal concentrations are obtained with the chemical collector. The residual Zn, Cu, and Pb are reduced by a factor of 13.7, 3.7, and 29.7, respectively, from the case with no collector added.

Effect of Collector Dosage on the Metal Removal

The effect of the collector type and dosage on the heavy metal removal was studied. The air flow rate was held constant at 12,150 cm³/min (0.429 ft³/min). The three chemical collectors (Nalco-7182, WOF-67, and Jayfloc-806) were each investigated separately, with the collector concentration ranging from 0 to 8.0 mg/L. During these experiments, the pH was held constant at 9.18. The col-

lector precipitation-adsorption behavior depends on the charge of the precipitated particles and the collector charge type. This phenomenon warrants further investigation by the authors. The results for a metal plating wastewater from the Toledo, Ohio, area are summarized in Table 2 for the induced and nozzle air flotation systems. The effects of collector type and dosage for other plating wastewaters from the Toledo area have been examined by the authors [8]; those results were similar to those presented in Table 2. No direct conclusion can be drawn about which collector performed best because each collector performed optimally at different dosages for the different metals. Nalco-7182 performed well on all the wastewaters studied. In most cases, WOF-67 obtained optimal metal removals at a dosage of about 5 mg/L; the removal of all three metals typically exceeded 80% with both the induced and nozzle air flotation systems. The other chemical collectors, Nalco-7182 and Jayfloc-806, were very efficient for heavy metal removal at dosages between 2 and 5 mg/L. For example, at these dosages for Nalco-7182, removal of Zn, Cu, and Pb averaged 90.8, 89.0, and 73.3%, respectively. For Jayfloc-806 at a dosage of 2 mg/L, removal of Zn, Cu, and Pb averaged 89.2, 91.5, and 90.3%, respectively.

On the basis of the results presented in Table 2, the optimal collector dosage for maximum metal removal varied for each heavy metal and each collector used; however, the optimal collector dosage typically was in the 2- to 5-mg/L range. For a collector dosage of 2 mg/L, removals of Zn, Cu, and Pb averaged 90.9, 93.0, and 84.5%, respectively.

Effect of Air Injection Rate

For this series of experiments, the pH was held constant at the optimal pH (about 9.18). Because it was easier to vary the air flow rate in the induced air flotation system than in the nozzle air flotation system, the induced air flotation system was employed and the rotor speed was varied. All three collectors were used at the dosage of 2 mg/L. The results shown in Table 3 for a wastewater spiked with heavy metals show that the air injection rate significantly affects the residual metal concentration. The

TABLE 2. EFFECT OF COLLECTOR TYPE AND DOSAGE ON HEAVY METAL REMOVAL AT PH 9.18 USING AN AIR INJECTION RATE OF 12,150 CM³/MIN FOR THE SUPREME-2 WASTEWATER USING WITH INDUCED AND NOZZLE AIR FLOTATION^a

Chemical Collector	Collector Dosage (mg/L)	Residual Metal Concentration (mg/L)					
		Induced System			Nozzle System		
		Zn	Cu	Pb	Zn	Cu	Pb
WOF-67	0	3.01	1.23	1.02	3.22	1.31	1.01
	0.5	1.92	0.55	0.48	1.56	0.94	0.85
	1.0	0.89	0.32	0.23	0.66	0.52	0.51
	2.0	0.42	0.09	0.18	0.54	0.18	0.39
	5.0	0.08	0.06	0.15	0.18	0.06	0.09
	8.0	0.52	0.03	0.39	1.74	0.03	0.87
Nalco-7182	0	3.67	1.16	1.34	2.84	1.13	0.98
	0.5	2.56	0.26	0.92	1.78	0.86	0.76
	1.0	1.18	0.06	0.76	1.02	0.41	0.24
	2.0	0.24	0.03	0.54	0.33	0.09	0.17
	5.0	0.06	0.09	0.18	0.14	0.06	0.10
	8.0	0.18	0.09	0.42	0.56	0.02	0.15
Jayfloc-806	0	2.35	0.47	1.41	2.73	1.39	1.21
	0.5	1.83	0.26	0.84	2.12	1.04	1.12
	1.0	0.48	0.17	0.36	0.82	0.78	0.48
	2.0	0.16	0.03	0.09	0.21	0.06	0.12
	5.0	0.03	0.03	0.06	0.08	0.03	0.02
	8.0	0.12	0.01	0.12	0.36	0.12	0.06

^a Initial metal concentrations: Zn_i = 3.94 mg/L, Cu_i = 1.58 mg/L, and Pb_i = 1.46 mg/L.

TABLE 3. EFFECT OF AIR INJECTION RATE ON RESIDUAL METAL CONCENTRATION USING 2 MG/L OF COLLECTOR AT PH 9.18^a

Chemical Collector	Rotor Speed (rpm)	Air Flow Rate		Residual Metal Concentration (mg/L)		
		cm ³ /min	ft ³ /min	Zn	Cu	Pb
WOF-67	900	9,710	0.343	10.04	1.91	4.89
	1,000	12,150	0.429	3.69	1.26	2.12
	1,100	13,080	0.462	5.73	2.20	3.39
	1,200	14,780	0.522	10.36	3.38	4.36
	1,300	16,990	0.600	12.04	4.56	5.44
Nalco-7182	900	9,710	0.343	12.06	4.13	3.10
	1,000	12,150	0.429	4.73	2.66	1.79
	1,100	13,080	0.462	4.12	1.52	4.41
	1,200	14,780	0.522	5.03	0.71	5.34
	1,300	16,990	0.600	5.16	1.86	6.12
Jayfloc-806	900	9,710	0.343	17.32	0.94	3.22
	1,000	12,150	0.429	5.31	0.78	1.62
	1,100	13,080	0.462	3.74	0.65	2.48
	1,200	14,780	0.522	4.48	0.82	3.08
	1,300	16,990	0.600	6.03	1.80	4.63

^a Initial metal concentrations: Zn_i = 25.0 mg/L, Cu_i = 25.0 mg/L, and Pb_i = 25.0 mg/L.

optimal rotor speed was determined to be about 1,000 rpm, corresponding to an air injection rate of 12,150 cm³/min.

For this air injection rate with WOF-67, the residual Zn, Cu, and Pb concentrations were reduced from an initial concentration of 25.0 mg/L to 3.69, 1.26, and 2.12 mg/L, respectively; removals thus exceeded 85.2%. With Nalco-7182, the residual concentrations of Zn, Cu, and Pb were 4.73, 2.66, and 1.79 mg/L, respectively, corresponding to removals of 81.1, 89.4, and 92.8%. With Jayfloc-806, the residual concentrations of Zn, Cu, and Pb were 5.31, 0.78, and 1.62 mg/L, respectively, corresponding to removals of 78.8, 96.9, and 93.5%.

Studies of Simultaneous Oil and Heavy Metal Removal

In the previous discussion, the emphasis was on the removal of heavy metals by joint precipitation and flotation methods; no effort was made to determine the residual oil in the water. The thrust in those preliminary studies were to determine the optimal conditions for the simultaneous removal of oil and heavy metals.

The oily emulsion in the wastewater was subjected to the same conditions as in the metal removal experiments. All three collectors were used at the various collector dosages (0.0, 0.5, 1.0, 2.0, 5.0, and 8.0 mg/L). The pH was maintained at the optimal condition (about 9.18) and the rotor speed was maintained at the optimal value of 1,000 rpm.

The results of these simultaneous removal studies are shown in Table 4. Comparisons between the metal removal studies and the simultaneous oil and heavy metal removal studies for Zn, Cu, and Pb are shown in Figures 7, 8, and 9, respectively. The effect of the collector type is likewise seen in these figures.

The joint precipitation and air flotation process is very effective for their removal of both oil and heavy metals from industrial wastewaters. For example, with the nozzle air flotation unit, the Nalco-7182 collector at a dosage of 12 mg/L, pH of 9.18, and air flow rate of 12,150 cm³/min, the residual oil concentration was 36 mg/L, corresponding to a removal of 86.2%. With the induced air flotation system, the Jayfloc-806 collector at a dosage of 8 mg/L, pH of 9.18, and an air flow rate of 12,150 cm³/min, the residual oil concentration was 21 mg/L, correspond-

ing to a 94.4% removal. Meanwhile, the removal efficiencies for the metals were close to the values obtained for the independent metal removal studies (as evidenced in Figures 7 through 9). As an example, residual Zn concentrations in the heavy metal removal studies were 0.33 and 0.16 mg/L for the induced air and nozzle air flotation systems, respectively, while residual Zn concentrations in the simultaneous metal-oil removal study were 0.31 and 0.12 mg/L, respectively.

Figure 7 shows that the minimum residual Zn concentration was obtained at a collector dosage of about 5 mg/L for both Nalco-7182 and Jayfloc-806. The residual Zn concentration is observed to increase for collector dosages greater than 5 mg/L; this behavior may be due to a charge reversal for the precipitates with increased collector dosages. This behavior is also seen in Figure 8 for Cu when using Nalco-7182. Figure 8 indicates that the minimum Cu concentration was obtained at a collector dosage of about 2 mg/L for Nalco-7182; the minimum Cu concentra-

TABLE 4. SIMULTANEOUS REMOVAL OF OIL AND HEAVY METALS AT PH 9.18 USING THE PRECIPITATION/AIR FLOTATION SYSTEM FOR THE SUPREME-2 WASTEWATER^a

Chemical Collector	Collector Dosage (mg/L)	Residual Concentration (mg/L)			
		Oil	Zn	Cu	Pb
Nalco-7182	0	261	3.11	1.36	1.10
	0.5	233	2.73	0.32	1.08
	1.0	194	1.36	0.07	0.56
	2.0	112	0.31	0.03	0.37
	5.0	92	0.12	0.06	0.23
	8.0	64	0.29	0.18	0.45
	12.0	36	0.47	0.39	0.82
Jayfloc-806	0	372	3.60	1.08	1.21
	0.5	268	1.77	0.38	0.69
	1.0	172	0.54	0.24	0.29
	2.0	148	0.12	0.05	0.11
	5.0	62	0.02	0.03	0.04
	8.0	21	0.09	0.03	0.09
	12.0	27	0.16	0.01	0.18

^a Initial wastewater conditions: Oil_i = 551.42 mg/L, Zn_i = 3.94 mg/L, Cu_i = 1.58 mg/L, and Pb_i = 1.46 mg/L.

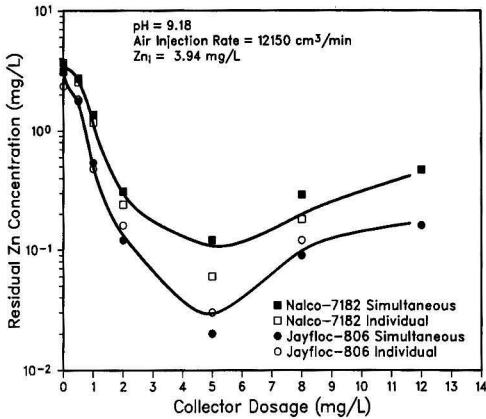


Figure 7. Effect of collector dosage on the removal of zinc in the precipitation/air flotation studies.

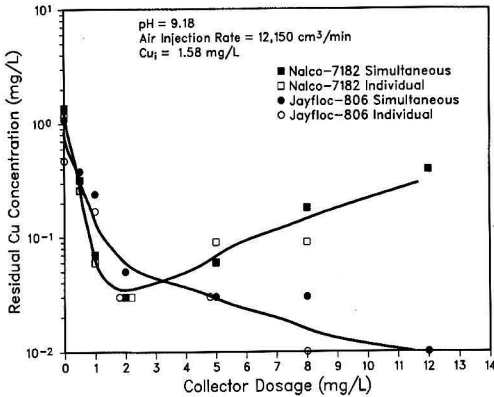


Figure 8. Effect of collector dosage on the removal of copper in the precipitation/air flotation studies.

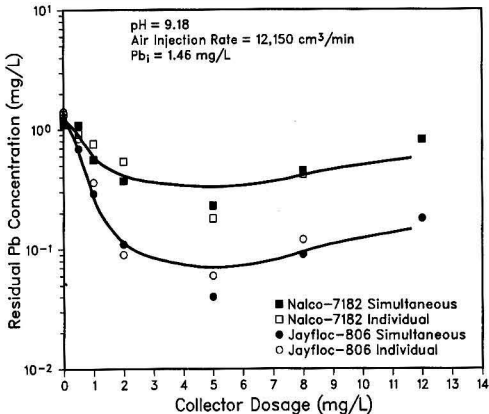


Figure 9. Effect of collector dosage on the removal of lead in the precipitation/air flotation studies.

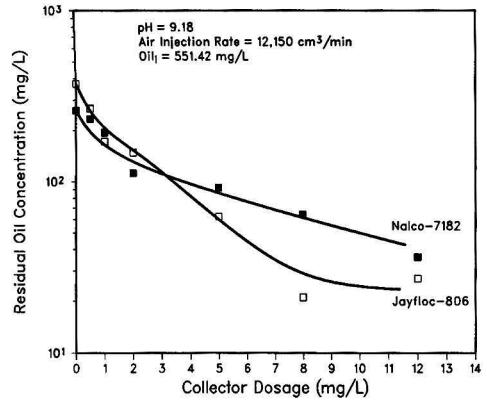


Figure 10. Effect of collector dosage on simultaneous removal of oil in the precipitation/air flotation studies.

tion was obtained at the maximum collector dosage used in this study (12 mg/L) with Jayfloc-806. Figure 9 shows that the minimum Pb concentration was obtained at a collector dosage of about 2 mg/L with both collectors.

Metal removal generally was slightly greater in the nozzle air flotation unit than in the induced air flotation unit. This result, however, does not categorically indicate that the nozzle unit outperforms the induced unit. The results do indicate that the nozzle unit produced more consistent metal removal results than did the induced unit. The reason for such behavior is not known.

Figure 10 shows the residual oil concentrations obtained by using this precipitation-flotation technique at various collector dosages. Two chemical collectors, Nalco-7182 and Jayfloc-806, were used in this portion of the study. Jayfloc-806 removed more oil than Nalco-7182, and the greatest oil removal obtained was 96.2% at a dosage of 8 mg/L Jayfloc-806.

The removal efficiencies of the heavy metals (Zn, Cu, and Pb) and oil are listed in Table 5 for various dosages of Nalco-7182 and Jayfloc-806. Table 5 also lists values of the enhancement ratio* for each of the heavy metals and oil. Of the two collectors, greater enhancement for Cu removal was observed with Nalco-7182, which provided greater selectivity for Cu. Jayfloc-806 had greater enhancement for removal of Zn, Pb, and oil. Figure 11 shows the enhancement ratio plotted as a function of the collector dosage for the two chemical collector systems. The enhancement ratio typically reaches a maximum for each component at a collector dosage in the range of 4-5 mg/L. Because the curves typically exhibit a concave downward shape, it would be possible to optimize the chemical collector dosage for maximum removal of any particular heavy metal.

SUMMARY AND CONCLUSIONS

The feasibility of using the joint metal hydroxide precipitation and air flotation system for simultaneous removal of heavy metals and oil was investigated using both batch laboratory induced and nozzle air flotation systems. Wastewaters from several industries in the Toledo, Ohio, area were used; these wastewaters contained Zn, Cu, Pb, and oily materials.

The residual metal concentrations were observed to be

* Enhancement ratio is defined here as: $(R = (C_i - C_{\text{with collector}}) / (C_i - C_{\text{without collector}}))$

TABLE 5. REMOVAL EFFICIENCIES AND ENHANCEMENT RATIOS FOR REMOVAL OF HEAVY METALS FOR TWO CHEMICAL COLLECTORS IN THE SIMULTANEOUS REMOVAL OF OIL AND HEAVY METALS^a

Chemical Collector	Collector Dosage (mg/L)	Metal Removal Efficiency (%)			Oil Removal Efficiency (%)	Enhancement Ratio ^b			
		Zn	Cu	Pb		Zn	Cu	Pb	Oil
Nalco-7182	0	21.05	13.9	24.65	52.65	1.00	1.00	1.00	1.00
	0.5	30.7	79.75	26.0	57.75	1.46	5.73	1.06	1.10
	1.0	65.5	95.55	61.65	64.8	3.11	6.86	2.50	1.23
	2.0	92.15	98.1	74.65	79.7	4.37	7.05	3.03	1.51
	5.0	96.95	96.2	84.25	83.3	4.60	6.91	3.42	1.58
	8.0	92.65	88.6	69.2	88.4	4.40	6.36	2.81	1.68
	12.0	88.1	75.3	43.85	93.5	4.18	5.41	1.22	1.77
Jayfloc-806	0	34.0	31.65	17.1	32.35	1.00	1.00	1.00	1.00
	0.5	55.1	75.95	52.75	51.4	6.38	2.40	3.08	1.59
	1.0	86.3	84.8	80.15	68.8	10.00	2.68	4.68	2.13
	2.0	96.95	96.85	92.45	73.15	11.24	3.06	5.40	2.26
	5.0	99.5	98.1	97.25	88.75	11.53	3.10	5.68	2.74
	8.0	97.7	98.1	93.85	96.2	11.32	3.10	5.48	2.97
	12.0	95.95	99.35	87.65	95.1	11.12	3.14	5.12	2.94

^a Initial wastewater conditions: Oil_i = 551.42 mg/L, Zn_i = 3.94 mg/L, Cu_i = 1.58 mg/L, Pb_i = 1.46 mg/L, and pH = 9.18.

^b Enhancement ratio is defined as: $R = [C_i - C_{\text{with collector}}] / [C_i - C_{\text{without collector}}]$.

a sensitive function of pH, flotation collector dosage, and air injection rate. An optimal pH of 9.18 was determined from jar tests and used in the various flotation runs. The optimal pH may differ from that determined above for other wastewaters, collectors, and air flotation systems. One collector dosage was not effective for all the wastewaters having different initial metal concentrations. The optimal air injection rate was determined to be about 12,150 cm³/min. Metal removals exceeding 80% were consistently achieved for the precipitation-flotation process, while oil removal as high as 96.2% was obtained at specific collector dosages and the optimal air injection rate. The removal of the various heavy metals and oil appears to be occurring through a coprecipitation-adsorption mechanism. The residual metal concentrations for the wastewaters subjected to this joint precipitation-flotation treatment were in all cases lower than the limits placed on industries by the Toledo Industrial Wastewater Pretreatment Program. The selectivity for a particular heavy metal or oil can be influenced by the use of a particular chemical collector and its dosage.

The above results show that this new, emerging technology has the capacity for simultaneously removing oil and heavy metals from solution. The advantages of this processing scheme are its simplicity, relatively low operating costs, and one-stage operation (in comparison, conventional processes use a two- or three-stage operation to remove the metals and oil separately). Although no chemical analyses were performed on the resulting foamate, such analyses are planned for future studies to determine the mass balances and composition of the foamate.

NOTATION

- C Metal (or oil) concentration (mg/L)
- C_i Initial metal (or oil) concentration (mg/L)
- Cu_i Initial copper concentration (mg/L)
- Oil_i Initial oil concentration (mg/L)
- Pb_i Initial lead concentration (mg/L)
- pH -log [H⁺]
- R Enhancement ratio, defined as:

$$R = \frac{C_i - C_{\text{with collector}}}{C_i - C_{\text{without collector}}}$$

Zn_i Initial zinc concentration (mg/L)

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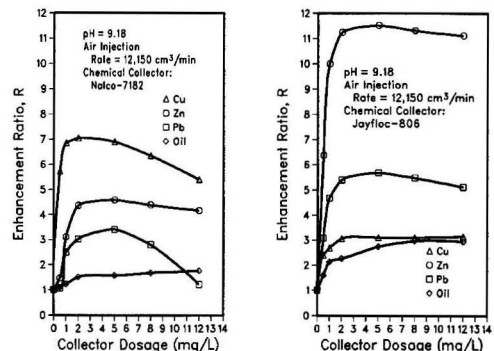


Figure 11. Enhancement ratios as a function of the collector dosage for the chemical collector systems: (a) Nalco-7182 and (b) Jayfloc-806.

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Lamella Settlers: Material Balances And Clarification Rates

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We show that material balances and clarification rates of a lamella settler can be obtained from the particle size distribution and density of the solid, the density and viscosity of the liquid, the desired concentration of solids in the overhead product, and the concentration of solids in the feed and underflow, using an algorithm based on a simple geometric model. The method was validated using concentrated suspensions (up to 20 vol% solids) of four different feed-particle size distributions of hydrargillite (aluminum hydroxide) in water. Most of the data were obtained in a 60-cm-long settler with 1-cm plate separation inclined at 60° to the horizontal in "open bottom" and "normal" configurations. The algorithm is not applicable to tube settlers, whose hydrodynamics are more complex.

INTRODUCTION

Lamella settlers are very effective sedimentation devices, low in energy intensity, which are being used extensively in water treatment plants and in some applications in the mining and minerals industry, but not as extensively in the chemical industry. They consist of a set of parallel plates into which a slurry is fed to obtain gravitational separation. The clarified liquid collects under each of the plates and flows upward to the overflow, and the solids settle and flow along the bottom of each plate to be collected in the underflow (Figure 1).

Lamella settlers can be used in place of other commonly used separation devices such as hydrocyclones, elutriators, thickeners, etc. They have several advantages over hydrocyclones, for example: (1) they are very low in energy intensity and in shear; (2) the ratio of overhead to underflow product can be changed at will, which allows selection of separation characteristics; and (3) the very low shear minimizes secondary nucleation and breakage of fragile crystals when the settler is coupled to a crystallizer. These reasons prompted our investigation into the applicability of lamella settlers to the crystallization of hydrargillite (aluminum hydroxide) in the aluminum-air battery [1].

The hydrodynamic flow in lamella settlers has been shown to be very complex. It has been treated by Leung and Probst [2, 3] and in numerous publications by Acrivos, Herbolzheimer, and Davis [4, 7]. Most aspects were reviewed in detail by Davis and Acrivos [8].

The analysis and data of Davis *et al.* [6] indicate that for steady-state operation the settler clarification rate is given by

$$Q = Uf(C)[1 + (H \sin \phi)/s]/\cos \phi \quad (1)$$

The treatment in Davis *et al.* [6] predicts the height of the

various regions in the settler. Equation (1) simply states that the clarification rate is the product of a suitably chosen particle-settling velocity multiplied by the hori-

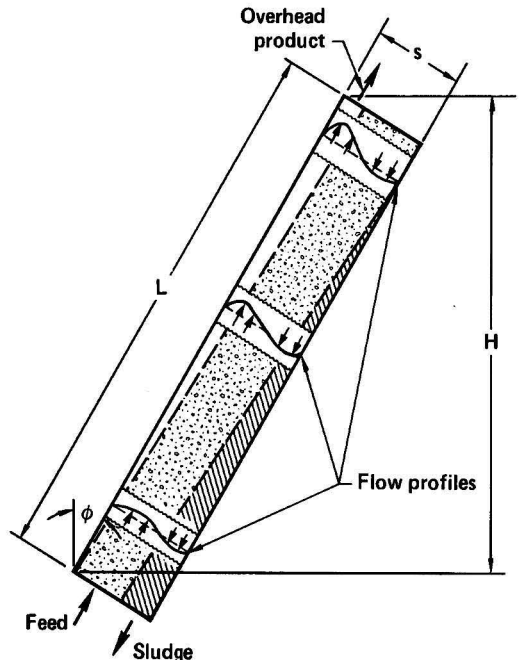


Figure 1. Lamella settler.

zontal projected area of the settler. The equation does not include the effects of the axial dispersion in a fluidized bed, [9] the effects of hydrodynamic instability and wave-induced mixing within the settler, [2-8] or the complex effects obtained in the fluidization of mixtures of particles with significantly different densities [10, 11].

In spite of the limitations of present models of lamella settlers, the practical application of such devices would benefit from being able to predict the clarification rates, material balances, and particle size distributions of the overhead and bottom products. This paper describes a simple algorithm that has been developed to estimate the clarification rates and material balances for monodensity particles suspended in a fluid. None of the presently available models allows calculation of product size distributions.

EXPERIMENTAL

The initial experiments were carried out using a settler and experiment design similar to that used by Leung [2]. The internal dimensions of the settler (Figure 2) were: length 60 cm, plate separation 1 cm, and width 5 cm. A flow splitter located in an end box at the bottom of the settler allowed for partitioning the settler flow channel for the feed and underflow streams; a propeller stirrer coupled to a variable-speed low-rpm motor provided agitation to the dense underflow slurry to keep it from plugging the outlet tube. The settler was mounted in a fixture that allowed it to be positioned at various inclinations to the horizontal. The settler was made from 3-mm-thick clear acrylic to allow visual observation and the determination of total solids content at various heights using x-ray transmission measurements.

The initial experiments were carried out in the "normal" configuration shown in Figure 3, which allows measurement of flow rates and composition of the overflow and underflow. The main problem in operating the settler in this configuration is the tendency for plugging of the underflow lines; the solids concentration in the underflow was consistently in the range 25-30 vol% for runs with 3% solids in the feed, and 38-43 vol% for runs with 20% solids in the feed. At flow-splitter heights greater than 1.5 mm above the bottom plate, the results were independent of splitter height.

Most of the experiments were performed using the open-bottom configuration of Figure 4, which only allows

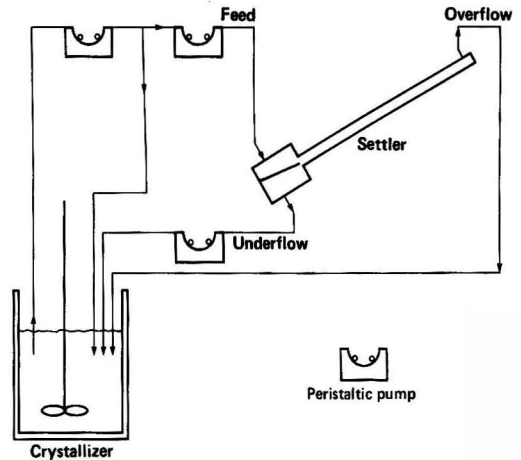


Figure 3. Normal-configuration settler flows.

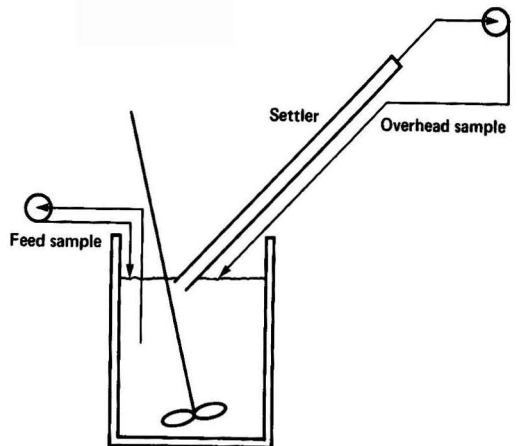


Figure 4. Open-bottom configuration settler flows.

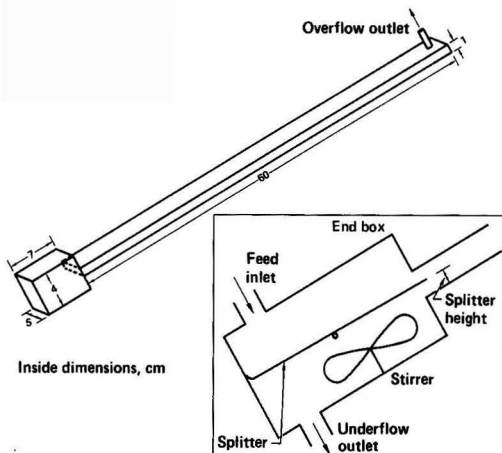


Figure 2. Plate settler, detail (dimensions in cm).

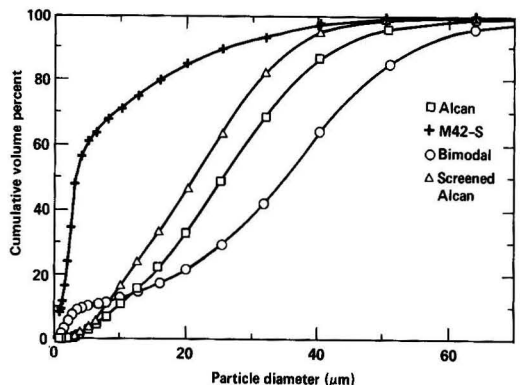


Figure 5. Comparison of particle size distributions.

for obtaining flow rates and samples from the overflow. In both the normal and open-bottom configurations, samples of the feed were obtained from a separate circulation loop. Great care was taken to ensure that the feed samples in the open-bottom configuration were representative of the material entering the settler. Waves were observed in the clear layer in virtually all the runs.

Aluminum hydroxide powder (hydrargillite grown from NaOH solutions, density 2.423 g/cm³) suspended in water was used in all the experiments. The four particle-size distributions used are shown in Figure 5. Two starting materials were used: commercial Bayer Process hydrargillite obtained from Alcan Aluminium Ltd., and a powder consisting primarily of fines (M42-S) grown in our laboratory. The two other size distributions were obtained by screening the coarsest material from the Alcan hydrargillite and by blending M42-S material with Alcan hydrargillite to obtain a bimodal distribution. The normal configuration was used only on Alcan hydrargillite; all other data were obtained in the open-bottom configuration.

The particle size distribution of the M42-S material was obtained by combining measurements on the very fine fraction made with a Sedigraph (x-ray, Model 5000D) with measurements on the entire population using a Coulter Counter Model TAI1; all other distributions were obtained using the Coulter Counter. For purposes of analysis the particles of hydrargillite were assumed to be spherical, although in reality the small crystals (<20 μm) are concretions of hexagonal plates and prisms, and the larger particles are irregular, roughly spherical agglomerates, with great variability from one particle to another (12, 13).

The data obtained in the normal configuration for an inclination of 60° to the horizontal ($\phi = 30^\circ$) are shown in Figures 6 and 7; only those data where the solids material balance closed within 3% are shown. Figure 6 gives the ratio of solids in the overflow, $Q_o C_o$, to solids in the feed, $Q_f C_f$, versus overflow rate Q_o . Figure 7 shows the ratio of solids concentration in the overflow to that in the feed, C_o/C_f , versus Q_o . Figure 7 also shows that there is very good agreement between data obtained in the normal and open-bottom configurations. A few experiments were carried out with the feed located at the top of the settler (cocurrent flow); the results are in good agreement with the rest of the data obtained in the normal configuration (bottom-fed countercurrent flow). The solid line in Figures 6 and 7 gives the calculated values obtained using the SETD algorithm to be described later.

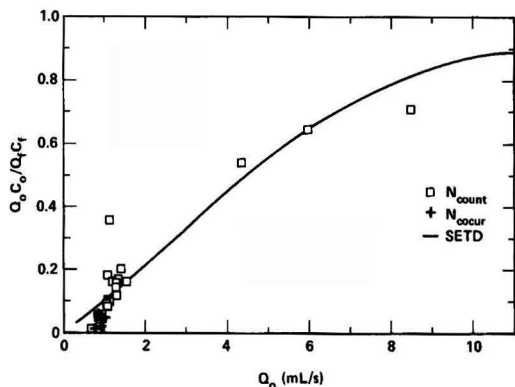


Figure 6. Comparison of overall settler material balances (normal configuration) with calculation ($\phi = 30^\circ$, $C_f = 0.2$). N_{count} = countercurrent flow (bottom-fed configuration); N_{occur} = cocurrent flow (top-fed configuration).

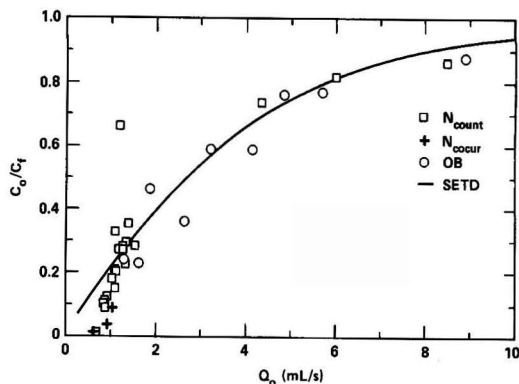


Figure 7. Comparison of observed ratio of solids concentration in overflow to that in feed with calculation ($\phi = 30^\circ$, $C_f = 0.2$). N_{count} = countercurrent flow (bottom-fed configuration); N_{occur} = cocurrent flow (top-fed configuration). OB = open bottom configuration.

The x-ray transmission measurements were made with the 88-keV radiation from a ¹⁰⁹Cd source, using Cu, Mo, and Al filters to remove the 22-keV component and various thicknesses of Al sheet for calibration. Representative results are shown in Figures 8 through 10. The results indicate that steady state was obtained in about one hour (Figure 8). The concentration profiles varied little from test to test; representative results with 3 vol% solids in the feed are shown in Figure 9, and with 20% solids in the feed in Figure 10.

Particle size distributions of the overflow were obtained for experiments in the normal configuration, with Alcan hydrargillite, 60° inclination to the horizontal, and 20 vol% solids in the feed. The results indicate that under these conditions the settler is not a very effective particle-classification device. Figure 11 shows the ratio of the volume of solids in the underflow product for a given Coulter size fraction, $Q_o C_o V_{up}$, to the corresponding volume in the feed, $Q_f C_f V_f$ (which is the usual way to express hydrocyclone efficiency [14]).

SETD ALGORITHM

The SETD algorithm is based on the simple model of Eq. (1): SETD assumes that all particles with a sedimentation rate smaller than U appear in the overhead product. Although the results shown in Figure 11 indicate that the assumption is not correct, the model does provide a basis for calculation.

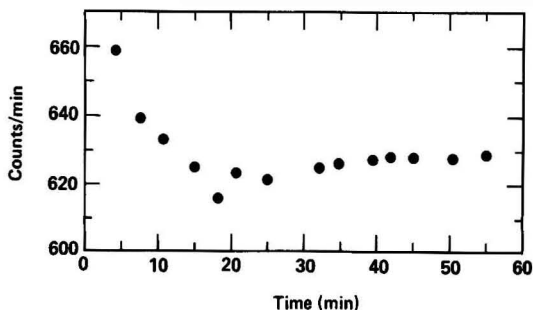


Figure 8. X-ray absorption measurement: time to attain steady state.

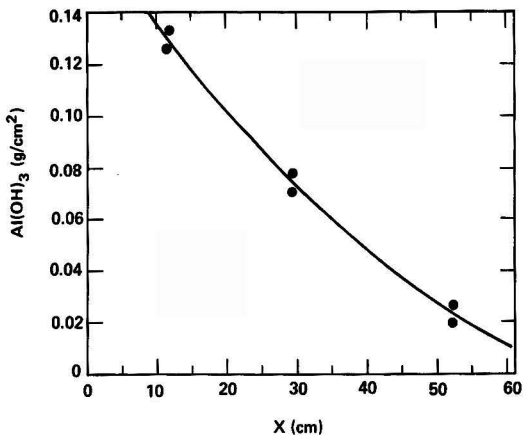


Figure 9. Total solids concentration in settler vs. position ($C_i = 0.03$, $\phi = 30^\circ$).

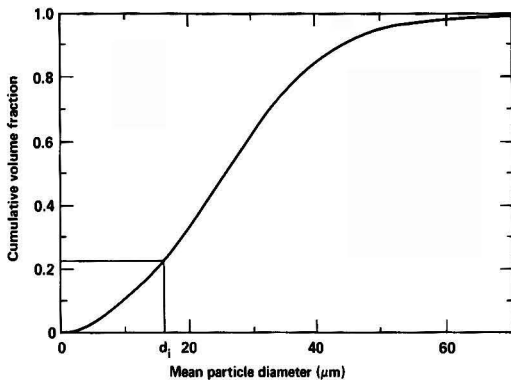


Figure 12. Feed-particle size distribution, showing the cut diameter d_i .

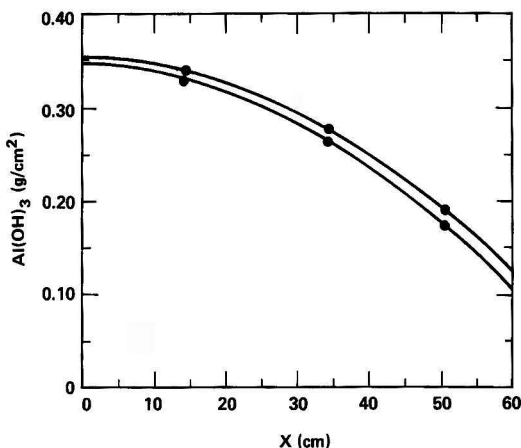


Figure 10. Total solids concentration in settler vs. position ($C_i = 0.2$, $\phi = 30^\circ$).

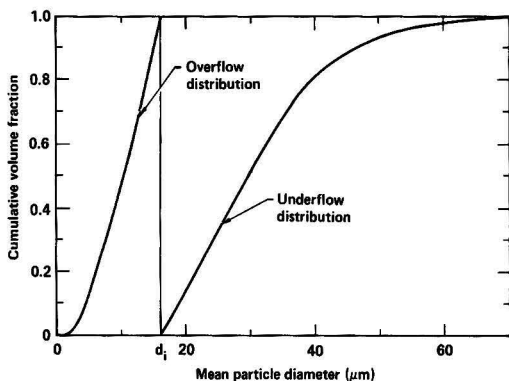


Figure 13. Particle size distributions of overflow and underflow for a perfect separator and a cut diameter d_i .

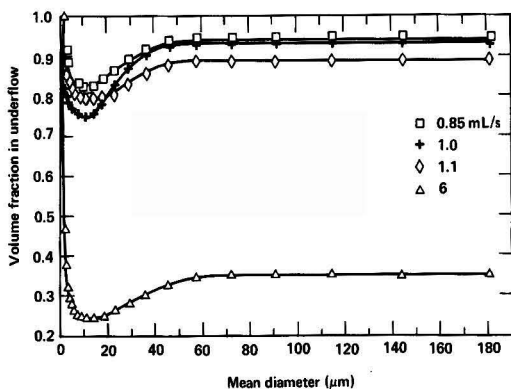


Figure 11. Separation efficiency of plate settler at $\phi = 30^\circ$, $C_i = 0.2$, vs. particle size for various overflow rates Q_o .

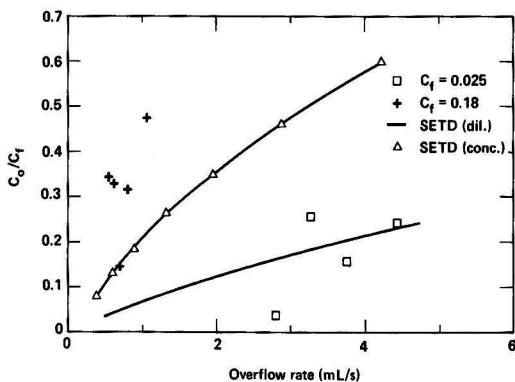


Figure 14. Comparison of normal-configuration data (50° inclination to horizontal) with calculation for C_i values of 0.025 and 0.18.

The experimental values of overhead flow rate and solids concentration are denominated Q_o and C_o ; the calculated values for a given particle size distribution Q_{oi} and C_{oi} , where i is the particle size index. A similar distinction is made for the underflow rate and solids concentration. The material balances for a settler with a feed rate Q_f , a feed-particle size distribution such as given in Fig. 12; for a given particle diameter d_i are

$$Q_f = Q_{oi} + Q_{ui} \quad (2)$$

and

$$Q_f C_f = Q_{oi} C_{oi} + Q_{ui} C_{ui} \quad (3)$$

which give the relations between the volumetric flow rates of slurry and solids, respectively.

A material balance for particles above and below d_i is given by:

$$Q_f C_f V_{fi} = Q_{oi} C_{oi} V_{oi} + Q_{ui} C_{ui} V_{ui} \quad (4)$$

Where the V 's are the cumulative volume fraction of particles smaller and equal to the diameter d_i , for the feed, over and underflow.

For an ideal settler, consistent with Eq. (1), the particle size distributions of the top and bottom product corresponding to the feed flow of Figure 12 are given in Figure 13. At the cut diameter d_c ,

$$V_{oi} = 1 \text{ and } V_{ui} = 0 \quad (5)$$

From Eqs. (4) and (5) one obtains

$$V_{fi} = Q_{oi} C_{oi} / Q_f C_f \text{ [for } d_i < d_c] \quad (6)$$

and from Eqs. (2), (3), (4), and (5)

$$C_{oi} / C_f = C_u V_{fi} [C_{ui} - C_f (1 - V_{fi})] \quad (7)$$

The free-particle settling velocity can be obtained using the algorithm given by Scott [15]:

$$J = 1308(D_s - D_f)D_i^3 / M_i^2$$

$$\text{if } J < 10, \text{ then } a = 24 \text{ and } b = 1$$

$$\text{if } 10 < J < 1000, \text{ then } a = 33.7J^{-0.19} \text{ and } b = 1.05J^{-0.05}$$

$$N_{re} = J^b / a$$

$$U = N_{re} M_i / (d_i D_i) \quad (8)$$

The above algorithm is dimensional (cgs units are required), and other values of a and b apply for $J > 1000$. The hindered settling velocity is obtained from Garside and Al-Dibouni [16]:

$$G = 0.1(N_{re})^{0.9},$$

$$N = 5.1 + 2.7G,$$

$$Uf(C) = U(1 - C)^{N-1} \quad (9)$$

Best fit to the data is obtained when the volume fraction of solids to be used in Eq. (9) is the geometric mean of the estimated overflow and feed volume fractions, i.e.,

$$C_{mi} = (C_{oi} C_{fi})^{0.5}, \quad (10)$$

and the diameter is the geometric mean diameter in the Coulter interval. The Coulter Counter measures the changes in resistance as the particles, suspended in an electrolyte, flow past two electrodes in a capillary. The changes in resistance are interpreted in terms of particle diameter. The Coulter Counter counts the number of particles within a given particle-diameter range. The size of the diameter ranges is not constant but increases by $2^{1/3}$ with increasing diameter; thus the mean diameter lies at a factor of $2^{1/6}$ from the upper and lower boundaries of the range.

The calculation starts by defining a series of particle diameters d_i for which the corresponding V_{fi} are obtained

from the feed-particle size distribution. The concentration of solids in the underflow is required for Eq. (7); it has to be determined for a given material and feed concentration. The results of the calculation are not very sensitive to C_{ui} ; the results shown in Figures 6 and 7 were calculated using $C_{ui} = 0.4$ for $C_f = 0.2$ and $C_{ui} = 0.27$ for the runs with $C_f = 0.03$.

Once the values of C_{ui} are known, the mean solids concentration is obtained from Eq. (10), the hindered settling velocity $Uf(C)$ from algorithms (8) and (9), and the clarification rate Q_{oi} from Eq. (1).

COMPARISON WITH EXPERIMENT

As illustrated in Figures 6 and 7, there is good agreement between data and the model but there are discrepancies at low and high flow rates (Q_o less than 1 mL/s or more than 8 mL/s). At low flow rates the mean solids concentration within the settler is lower than the geometric mean indicated by Eq. (10). At high flow rates the model consistently predicts higher solids concentrations in the overflow than found experimentally. It is likely that the reason for the discrepancy is that many of the finer particles are trapped and are removed by the underflow.

While Eq. (1) predicts larger separation when the settler is nearly horizontal, our results at 50° inclination to the horizontal indicate that, at 18 vol% solids in the feed, the settler was being plugged by underflow solids (Figure 14); there is reasonably good agreement between the model and experiment at 3 vol% solids in the feed. Two experiments at 40° inclination showed performance much worse than predicted by the model, indicating that the solids in the underflow were being retained within the settler.

The experiments using M42-S material (Figure 15) show good agreement with the model at high flow rates and 20 vol% solids in the feed, but considerable deviation

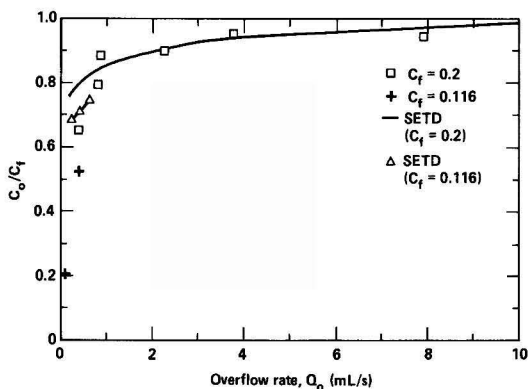


Figure 15. Comparison of open-bottom data for the M42-S distribution with calculation ($\phi = 30^\circ$, $C_f = 0.116$ and 0.2).

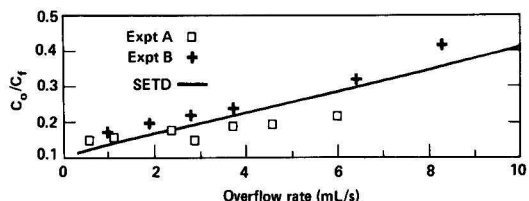


Figure 16. Comparison of two sets of data obtained for the biomodal distribution with calculation ($\phi = 30^\circ$, $C_f = 0.2$).

at low flow rates, particularly for 11.6 vol% solids in the feed. There was good agreement between model and experiment for the bimodal population and 20% solids in the feed, as shown in Figure 16.

It should be pointed out that the calculated results are very sensitive to errors in the measurement of particle size distribution. For example, good agreement was found between the model and M42-S data when the particle size distribution was measured with a Sedigraph, as compared with poor agreement when the distribution was measured with another instrument. In the case of the bimodal distributions, care was needed to obtain reproducible results because of the range of particle sizes and the nature of the distribution. Although no data were obtained using the screened Alcan distribution with the plate settler, results for this distribution using tube settlers indicate that the data were consistent with data for the other distributions studied.

ACKNOWLEDGMENTS

Professor Edward Grens, University of California, Berkeley, extended the model of Leung and Probststein [2] to include the case of having solids in suspension in all three layers. Andrew T. Anderson obtained all the data in the normal settler configuration; Steven A. Muelder obtained most of the data in the open-bottom configuration. The work was done under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

NOMENCLATURE

a, b	Constants, Eq. (8)
C	Solids concentration (volume fraction)
d	Particle diameter
D	Density
G	Intermediate value, calculation of hindered settling velocity
H	Settler height
J	Intermediate value, calculation of hindered settling velocity
M	Viscosity
N	Intermediate value, calculation of hindered settling velocity
N_{Re}	Reynolds number of free-settling particle
Q	Flow rate
s	Spacing between the settler plates
U	Free-particle settling velocity
V	Cumulative volume fraction of solids in the particle size distribution

Subscripts:

i	Particle size index
f	Feed
l	Liquid property (particle-free)

m	Geometric mean
o	Overflow, top product
S	Solid property
u	Underflow, bottom product

Greek letters:

ϕ	Angle of settler to the vertical
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Aquifer Restoration: Chlorinated Organics Removal Considerations in Proven vs Innovative Technologies

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The arguments over the use of proven vs. innovative technologies have gone on since the inception of the scientific and engineering communities. Currently, the discussions and interactions regarding "applicable" technology and when and where to use it focus on groundwater contamination. The need for removal of chlorinated organic compounds looms large as one of many groundwater treatment problems. Widely accepted technology keys on carbon as the solution; however, carbon is not without problems. Alternative innovative approaches include volatilization and biologic degradation. The alternatives have applicability and also certain limitations.

INTRODUCTION

The vulnerability of our groundwater resources has become clear in recent years. Leaks from underground tanks and piping and even single-event surface spills of relatively small volumes of organic material can contaminate millions of gallons of groundwater. A case study is used to compare the relative costs of remediation by carbon adsorption and air stripping. The technical feasibility of remediation through enhanced biological degradation is also discussed.

CARBON ADSORPTION

The process of adsorption onto granular activated carbon (GAC) involves contacting the groundwater stream with the carbon, usually by flow through a series of packed bed reactors. The activated carbon adsorbs hazardous organic constituents by a surface attraction phenomenon in which organic molecules are attracted to the internal pores of the carbon granules. Adsorption depends on the strength of the molecular attraction between adsorbent and adsorbate, molecular weight, type and characteristics of adsorbent, electrokinetic charge, pH, and surface area. Once the micropore surfaces are saturated with organics, the carbon is "spent" and must either be replaced with virgin carbon or be regenerated. The time to reach "breakthrough" or exhaustion is the single most critical operating parameter.

Activated carbon is an effective and reliable means of removing low-solubility organics. It is suitable for treating a wide range of organics over a broad concentration range. It is not extremely sensitive to changes in concentrations or flow rate and, unlike biological treatment,

is not adversely affected by toxics. However, it is quite sensitive to suspended solids and oil and grease concentrations. Carbon systems are typically run in a series operation. When the first bed becomes spent, the second bed remains available for treatment of the stream, becoming the primary bed. The first is then regenerated in place, on-site, or off-site. A case study is used to illustrate this point and to compare technologies.

Design calculations for a 158 liters per second case have shown that 286 cubic meters of carbon would be needed for each bed in order to maintain a 30-minute contact time. Table 1 presents the organic contamination used in this example. Carbon adsorption capacities were theoretically estimated using single solute isotherm data for each compound. These estimates ignore potential competitive effects in a multicomponent mixture. Design of a full-scale system should be preceded with laboratory and, if possible, pilot studies. Approximately 6,220 kg/day of carbon would be consumed in the full-scale system.

With this large carbon demand, an on-site regeneration facility would clearly be a more cost-effective alternative for regeneration. Options include a steam or thermal regenerating facility. Thermal reactivation could be used to achieve nearly complete recovery of carbon capacity. An afterburner would be employed to oxidize the organic compounds fully, and a scrubber might be employed to clean the air of any HCL formed from the combustion of chlorinated hydrocarbons. Average HCL emissions would be equivalent to levels discussed later for fume incineration of air stripping effluent. Thermal regeneration and off-gas scrubbing would add a significant capital cost onto the cost of the basic treatment system. The carbon adsorption system conceptual design for the treatment of groundwater is shown in Figure 1.

TABLE 1. INFLUENT ORGANIC CONCENTRATIONS AND ESTIMATED CARBON CAPACITIES FOR CASE STUDY

Compounds	Influent Concentration (ppb)	Carbon Capacity (mg/g)	Carbon Consumption per Unit of Groundwater (mg/g)
Carbon Tetrachloride	7500	60	.129
Chloroform	250	0.9	.292
Chlorobenzene	550	51	.011
Dichlorobenzene	5500	260	.020
Trichlorobenzene	500	120	.004
TOTAL			.456

NOTE: Capabilities based on isotherms from EPA-600/8-80-023, Carbon Adsorption Isotherms for Toxic Organics. Values are based on expected concentrations, assuming the single solute isotherm applies. Actual removals may be less due to preferential removals within a multi-specie solution. Units given in mg of solute adsorbed per gram of carbon.

TABLE 2. COSTS FOR GROUNDWATER TREATMENT BY CARBON ADSORPTION

CAPITAL COSTS	
Carbon Adsorption System	\$ 1,400,000
Pump Station	150,000
Regeneration System	1,747,000
TOTAL	\$ 3,297,000
OPERATIONS AND MAINTENANCE (ANNUAL COSTS)	
Adsorption System	
Power (\$.04/kwh)	\$ 17,000
Labor (\$40,000/man-yr)	30,000
Regeneration Systems	
Maintenance	\$ 11,600
Power (\$.04/kwh)	12,000
Fuel (\$4.73/29 cu m)	80,000
Makeup Carbon (8%, \$2.86/kg)	547,200
Labor (\$40,000/man-yr)	560,000
TOTAL	\$ 1,257,800
PRESENT WORTH¹	\$11,020,000

NOTES:
¹1986 \$; 10% interest; 10 years of use.

COSTS

The costs for a carbon adsorption system are presented in Table 2 [1]. Costs were calculated for a GAC carbon adsorption system with thermal regeneration. Results presented in this table indicate that this process is both capital and operating cost intensive. The most significant operating cost component is makeup carbon to replace that lost to generation of fine particles or combustion in the regeneration process.

AIR STRIPPING

Using this alternative, groundwater from production and/or recovery wells is pumped at a rate of 3.6 MGD to an air stripping tower and sprayed upon a bed of high surface area/volume packing material. A blower provides a counter-current flow of fresh air through the packed bed to enhance volatilization of organic components. A typical air stripping installation applicable to the treatment of contaminated groundwater is depicted in Figure 2.

Air stripping has been used successfully in many applications nationwide to treat waters containing organic compounds. It has been used for streams containing low levels of organic compounds which could not support biological treatment. Stripping efficiency is dependent

upon vapor-liquid equilibrium distribution and mass transfer coefficient. Generally, compounds with higher vapor pressure and low solubility in water are more efficiently stripped. The Henry's Law Constant, a measure of the equilibrium distribution between air and dilute solutions, is typically used as an indicator of strippability [2].

Based on the significantly lower Henry's Law Constant for dichlorobenzene, its relatively low vapor pressure, and its high initial concentration, this compound becomes the height-determining factor for the air stripping tower in this example [3-4]. It should be noted that trichlorobenzene has a normal boiling point above 200°C and would typically be removed with patented steam stripping technology [5]. Many parameters, in addition to strippability, can be used to determine tower height, including air and water discharge limitations. The hydraulic flow rate was used to size the tower diameter, and an air flowrate/water flowrate ratio of 15:1 and a water flowrate/tower cross-sectional area of 20:1 were chosen to ensure required removal efficiencies.

Due to the high removal efficiency of the tower (>97 percent) and the high volumetric throughput, the vapor mass emission rate is expected to exceed .13 kg/min. This discharge could result in the regulatory requirement for installation of a emission control system. Currently, vari-

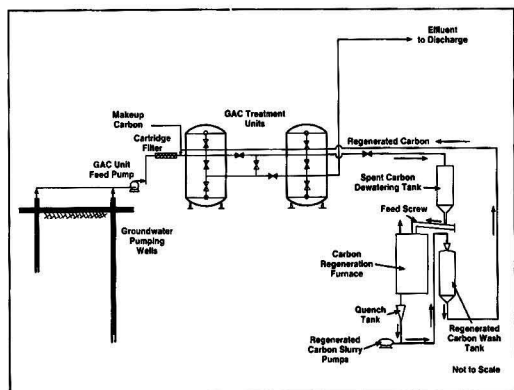


Figure 1. Typical granular activated carbon installation for groundwater treatment with thermal regeneration.

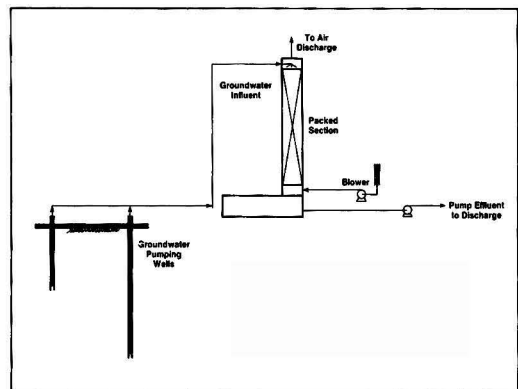


Figure 2. Typical air stripping installation for groundwater treatment.

ous states have no regulations specifically addressing this type of discharge, and a case-by-case evaluation can be expected. As a result, it is possible that discharge from a proposed new air stripping facility could be required to meet the Best Available Technology guidelines and/or conduct an exposure assessment.

Emission control options for this designed stripping unit were evaluated. The three options for emission control of the air stripper vapor effluent are: 1) direct venting to the atmosphere, 2) fume incineration, and 3) vapor phase carbon treatment. A discussion of each of these options follows:

- **Direct Venting:** Venting of the air stripper vapor effluent will result in a continuous emission of 17.5 lb/hr of chlorinated hydrocarbons. The acceptability of this option may ultimately depend upon results of air emission modeling, exposure assessment studies, and the cost-effectiveness evaluations conducted on other options.
- **Fume Incineration:** Fume incineration is used for gaseous emissions containing combustible species. The combustion of chlorinated hydrocarbons results in the formation of CO_2 , H_2O , and hydrochloric acid, as well as NO_x , CO , and other constituents formed as byproducts of combustion.
- **Vapor Phase Carbon Adsorption:** Carbon adsorption is widely used for the removal of organic compounds from air emission streams. The carbon adsorption system utilized in this design will incorporate carbon regeneration by using steam to raise the bed temperature and sweep the liberated organics from the bed. Contaminated water can be recirculated as feed to the carbon columns. The typical installation requires low-pressure steam, cooling water, and power (see Figure 4).

In addition, the following technologies can be considered: 1) boilers as fume incinerators, 2) vapor condensation, 3) vapor/liquid absorption, and 4) endothermic flaring.

COST ANALYSIS

Any restoration option must be implemented and operated in a cost-effective manner in addition to addressing the environmental concerns successfully.

The present worth (or present value) method (1986 dollars basis) was utilized to evaluate the total cost of each air stripping option. The costs of the various options can be compared based on total present worth. The following options were evaluated: 1) air stripping with fume incin-

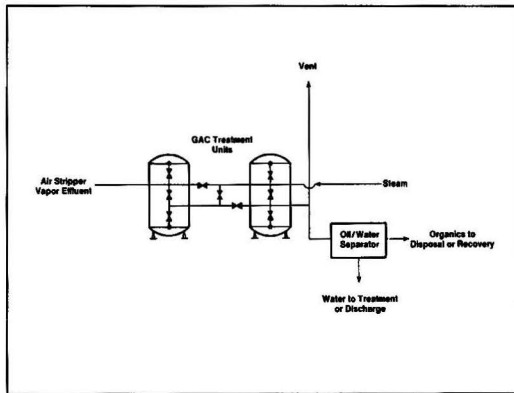


Figure 4. Preliminary conceptual design for vapor phase carbon adsorption.

eration and off-gas scrubber, 2) air stripping with fume incineration without off-gas scrubber, and 3) air stripping with vapor phase carbon treatment.

Air Stripping: Table 3 presents the estimated costs for this option. This analysis, as well as all other cost calculations in this subsection, is based on an interest rate of 10 percent and 10 years of use.

Air Stripping with Fume Incineration, With and Without Off-Gas Scrubbing: The costs for this option were developed by cost analysis of the two fume incineration cases. Table 4 presents the estimated additional costs over air stripping alone for this option. This table clearly shows the differential cost associated with the off-gas scrubbing system. Construction of the off-gas system greatly increases the complexity and capital cost of the fume incinerator. Estimated HCL emissions without off-gas scrubbing are .12 kg/min. This level is likely to trigger control requirements based on potential acid vapor effects. The present worth for the case utilizing acid gas scrubbing is approximately 26 percent higher than the case without.

Air Stripping with Vapor Phase Carbon: Table 5 presents the additional costs for this option over air stripping alone. This is the lowest cost option for control of air emissions from air stripping and yet adds four times the present worth cost of the basic air stripping system.

COMPARISON AND SELECTION OF COST-EFFECTIVE GROUNDWATER CONTROL/TREATMENT

Either a carbon adsorption or air stripping unit could be constructed to remove organic compounds from the example 3.6 MGD flow stream successfully.

Various institutional factors include permitting and, in particular, air emissions considerations. Air stripping results in the generation of an air emission composed of the organic compounds contained in the groundwater influent. Several options evaluated for air emission control could reduce emissions, should Best Available Technology (BAT) be applied but at a major increase in cost.

Liquid phase carbon adsorption has the advantage of achieving low air emission rates due to organic compound oxidation in the regeneration/afterburner process. All alternatives can successfully and dramatically reduce groundwater contaminant concentrations.

A major factor in selecting the most effective alternative is cost. Table 6 shows a cost comparison of the possible groundwater treatment alternatives based on capital, operating cost and present worth. Air stripping with direct

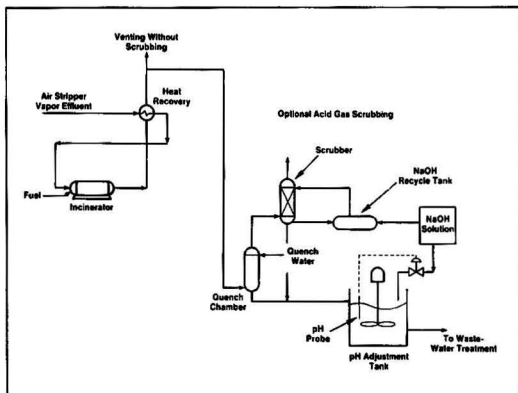


Figure 3. Conceptual design for fume incineration.

TABLE 3. COST FOR GROUNDWATER TREATMENT BY AIR STRIPPING

	CASE I
CAPITAL	
Air Stripping Unit (includes construction, delivery, blower, pump, engineering and contingency)	\$383,700
OPERATION AND MAINTENANCE	
Power (30 hp Fan, 40 hp pump # \$0.04/kwh)	\$ 18,400
Labor (\$40,000/man-yr)	8,000
Maintenance (6% of capital)	23,000
TOTAL PRESENT WORTH¹	\$ 49,400 \$687,000

¹1986 \$; 10 percent interest; 10 years of use.

TABLE 4. ADDITIONAL COST FOR AIR STRIPPER EMISSION CONTROL BY FUME INCINERATION

	CASE I ¹	CASE II
CAPITAL COSTS		
Fume Incinerator (construction, piping, contingency and engineering for incinerator and caustic tank, if needed)	\$ 2,950,000	\$1,595,000
OPERATION AND MAINTENANCE (ANNUAL COST)		
Power (\$.04/kwh)	\$ 12,600	\$ 6,300
Fuel (\$4.73/29 cu m Natural Gas)	1,060,700	1,060,700
Labor (1 man year)	40,000	40,000
Maintenance (6% of Capital)	174,000	95,700
Caustic (20% Soln @ \$.44/kg)	29,600	0
TOTAL O&M	\$ 1,316,900	\$1,202,700
ANNUAL COST PRESENT WORTH²	\$11,036,000	\$8,980,000

NOTES:

¹Case I assumes gases will be scrubbed before discharges, Case II does not. Both cases assume 70 percent heat recovery.

²1986 \$; 10 percent interest; 10 years of use.

TABLE 5. COSTS FOR AIR STRIPPER EMISSION CONTROL BY VAPOR PHASE ACTIVATED CARBON

CAPITAL	
Carbon Adsorption/Stream Regeneration Unit (commercial package unit) with Air Preheat Exchanger (includes construction, piping, contingency and engineering).	\$1,085,000
OPERATIONS AND MAINTENANCE (ANNUAL COST)	
Power (\$.04/kwh)	\$ 31,500
Steam (\$8/45 kg) ¹	216,600
Labor (\$40,000/man-yr)	40,000
Transport/Disposal of Pure Phase VOC (assumes phase separation/recycle of aqueous phase)	72,200
Maintenance (6% of Capital)	65,100
TOTAL	\$ 425,400
PRESENT WORTH²	\$3,697,000

NOTES:

¹Includes air preheating—may be reduced by optimization.

²1986 \$; 10 percent interest; 10 years of use.

discharge is by far the least expensive alternative. The addition of emission controls drives the cost up an order of magnitude to approximately the level of liquid phase carbon adsorption.

BIOLOGICAL DEGRADATION

Unlike carbon adsorption and air stripping, the use of biodegradation as an aquifer restoration technique involves the interaction of living microbes with the subject contamination. Biological reactors above ground and *in situ* processes are in use utilizing both aerobic and anaerobic bacteria, as well as natural and alien bacteria. Natural biodegradation can be an effective remedial response when enhanced with appropriate supplies of nutrients and oxygen, which supply energy for certain species of microorganisms. These microorganisms feed upon the organic contamination and release carbon dioxide, water, and byproducts. The rate of contaminant consumption is proportional to the total population of these microorganisms and the degree to which they effectively utilize the contamination as a food source. After contact with in-ground contamination the bacteria may adapt with the contaminant-utilizing species increasing in number. Stimulating the growth of these contaminant-utilizers is the job of the microbiologist and engineer.

The use of biological degradation is a relatively new tool for aquifer restoration; however, the advantages, disadvantages, difficulties and successes are becoming clearer. Biodegradation *in situ* is hindered by the following microbiological, hydrogeological, and chemical factors:

- Microbial activity relies on intimate contact of bacteria with contamination. Geological formations such as aquitards of any low permeability stratum may serve to separate bacteria from contamination. The utilization of natural bacteria may be more successful than foreign strains under such demanding conditions. It is postulated that natural bacteria, by virtue of multiple generation on-site, may penetrate the fine interstices of low permeability soils more readily than foreign bacteria.
- Soil/water chemistry effects the activity of microbes. Depending on temperature, pH, EH and other factors natural bacterial action may be adversely effected. The presence of the contaminant itself may produce toxic conditions rendering the bacteria dormant. Revival can often occur or be accomplished by appropriate application of nutrients and oxygen. The presence of too little contamination can hinder biological activity. Depending on site-specific factors, a floor of 1-10 ppm may be found.
- Natural bacteria, as well as foreign bacteria are often subject to predation by protozoan. These micropredators are generally introduced into the *in*

TABLE 6. COST COMPARISON FOR GROUNDWATER TREATMENT ALTERNATIVES

Alternative	Capital Cost	Annual Operation Maintenance Cost	Present Worth ¹
Air Stripping	\$ 383,700	\$ 49,400	\$ 687,000
Air Stripping/ Fume Incineration ²			
w/scrubber	3,433,700	1,366,300	12,013,600
w/o scrubber	1,978,700	1,252,100	9,667,000
Air Stripping/ Vapor Phase Carbon ³	1,468,700	474,000	4,379,000
Carbon Adsorption	3,297,000	1,257,800	11,020,000

¹ 1986 \$; 10 percent interest; 10 years of use.

² Cost of \$14,500/ton, \$11,800/ton, \$4,800/ton of air emissions abated result for Fume Incineration w/Scrubber, w/o Scrubber, and for Vapor Phase Carbon respectively, based on present worth for 10 years of operation.

³ Does not include groundwater recovery system costs.

situ ecosystem via the well casing during well installation. Enhancing the bacteria population can often overcome this drawback.

- *In situ* contaminant-utilizing bacteria must often compete with noncontaminant-utilizers for available food and oxygen. Attempts can be made to identify preferable species and customize the nutrient mix. Elimination of noncontaminant-utilizers is usually not possible.
- Supply of nutrient and oxygen *in situ* often creates a zone of high activity with elevated concentration of bacteria, nutrients and oxygen at the site of introduction. From the localized region oxygen transport can be restricted. Increased oxygen feed and/or multiple feed locations can often overcome this phenomenon.

The advantages of biological treatment compared to carbon and air stripping are often substantial and dramatic. Biological treatment at its best can be cost-effective, nonpolluting and have relatively little impact on above-ground activity. Recent studies confirm the viability of remediation by biodegradation.

Results of preliminary testing done at the labs of Groundwater Technology (Chadds Ford, Pennsylvania) on groundwater contaminated with trichloroethylene (TCE) are positive [6]. Naturally occurring bacteria were identified and the population enhanced using a custom blend of nutrients, including phosphorus and nitrogen compounds. The mix was oxygenated and the concentration of TCE was reduced from 7 ppm to less than 1 ppm in 6 days.

Laboratory and pilot plant studies utilizing anaerobic bacteria have been done by Boyer, et al [7] on a spill of 1,1,1-trichloroethane (TCA) at the site of a defunct electronics manufacturing facility. Six modified laboratory soil columns were utilized, volatilization losses were minimized, and ethanol was used as an additional carbon source. After 60 days the influent concentrations for TCA and ethanol were 20 ppm and 100 ppm, respectively. For 20 subsequent days the TCA effluent concentration did not exceed 20-50 ppb. Most samples taken for analysis showed less than 20 ppb (the detection limit). Effluent pH declined and then rebounded between days 20 and 40 indicating development of an acclimated microbial population. Visual inspection of the columns indicated the presence of bioslime.

Laboratory and field studies undertaken by Dr. Ralph Portier of Louisiana State University are currently

underway at the site of a waste oil recycling facility [8]. Preliminary results indicate that biological degradation on a large scale can result in removal efficiencies of 90-96 percent. Chemical analysis of the treated effluent show that the relatively more toxic contamination, in this case carbon chains less than C17, are preferentially converted. Initial costs of \$40/cu yd were estimated for the process (versus costs expected to exceed \$100/cu yd for off-site disposal).

CONCLUSIONS

Air stripping, carbon adsorption, and biological degradation of chlorinated hydrocarbon compounds have all shown success as remediation strategies. The alternatives each have advantages and disadvantages which can be evaluated only on a case-by-case, site-by-site basis.

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Pilot Process Variable Study of Coolside Desulfurization

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The Coolside desulfurization process is a dry sorbent injection technology developed for retrofit SO₂ control in coal-fired utility power stations. The process is low in capital and space requirements since, in its ideal configuration, the existing ductwork and particulate collector are used as the SO₂-sorbent reaction spaces. It has been developed through laboratory and 1 MW-scale field tests using hydrated lime as the primary process sorbent by Consolidation Coal Company (Consol). The field work showed promising results with observed SO₂ removal ranging up to 80%. In order to optimize the process performance through improved understanding of the process fundamentals, Consol constructed and is operating a 0.15 MW pilot test unit. This paper describes the results of a process variable test program, a first series of tests made in the pilot unit, and the unit operability observed during the test work.

INTRODUCTION

Coolside desulfurization is an SO₂ control technology involving dry sorbent injection followed by flue gas humidification by evaporation of water sprays. Conceptually, the technology would employ the existing or modified ductwork and particulate collection system (ESP or baghouse) as the SO₂ capture zones, resulting in a low installed capital cost and short construction time relative to conventional wet scrubbing (FGD). Coolside desulfurization, therefore, would be particularly well-suited for retrofit applications in coal burning power stations that lack adequate space for FGD installation or that have limited remaining boiler life. Coolside SO₂ removals of up to 80% have been measured in 1 MW field tests [1]. Demonstration tests (100 MW-scale) at the Ohio Edison Edgewater station under the DOE Clean Coal Technology Program are planned to begin in 1988. Participants in the program are the State of Ohio, Ohio Edison, Babcock & Wilcox and Consolidation Coal.

Based on the field tests and economic/engineering assessments, Consol has identified two areas of development needs for the Coolside technology to find broad applicability and acceptance, these are sorbent utilization and humidifier design/operability. In order to carry out the needed development work, Consol built a 0.15 MW pilot unit. The process variable tests reported in this paper were the first series of tests made in the pilot unit. The objective of the variable tests was to establish the reliability of the unit operation and test data before more extensive process/sorbent improvement work is done.

Process Description

Coolside desulfurization technology involves hydrated lime injection, flue gas humidification with water sprays and additive injection with the humidifying water into the ductwork downstream of the air preheater (Figure 1). SO₂ is removed by the entrained sorbent particles in the ductwork and by the dense sorbent bed collected in the particulate removal system. The humidification water serves a dual purpose. First, it activates the sorbent to enhance SO₂ removal and, second, it conditions the flue gas for more efficient ESP performance by lowering the gas resistivity. Since the residence time of the entrained sorbent in the ductwork is very short (up to a few seconds), SO₂ removal during the entrainment requires a highly active sorbent. The sorbent activity is significantly enhanced by the injection of soluble additives with the humidifying water. Laboratory sorbent studies indicate that hydrated lime sorbent activity can be improved by 50-100% with the use of additives and/or by controlling lime hydration conditions [2]; these are relatively simple and cost-effective measures. In addition, sorbent recycling is possible if the particulate collector can handle the resulting increased solids loading. This can significantly reduce the Coolside SO₂ control cost by lowering the fresh sorbent requirements.

An alternative would be boiler limestone injection (BLI) activation, which involves humidification and, optionally, additive injection to achieve additional SO₂ removal while the boiler is operating with limestone/lime injection (Figure 2). The BLI fly ash contains unreacted

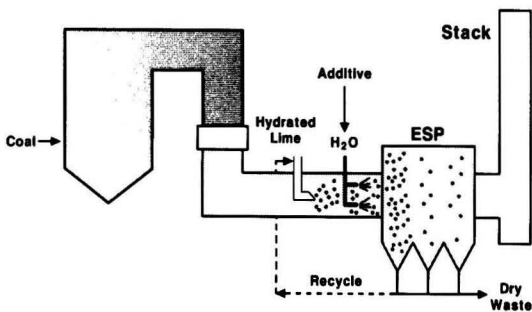


Figure 1. Coolside hydrated lime injection.

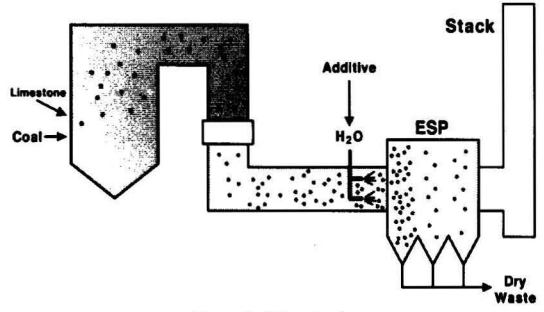


Figure 2. BLI activation.

CaO because the calcium utilization in the limestone injection process is low, ca. 20%. BLI activation uses this unreacted CaO for SO₂ removal by humidification and additive injection. Again, humidification serves the dual purpose of sorbent activation and flue gas conditioning for improved ESP performance. Although BLI may be limited in its application because of potential boiler derates, it allows the use of less expensive limestone as the sorbent. Thus, BLI activation may, in some cases, provide the lowest SO₂ removal cost.

1 MW Field Tests

Field tests were made using a pilot humidifier and ESP on a 3000-4000 acfm (1 MW equivalent) flue gas slipstream from a coal-fired industrial boiler located at Du Pont's Nylon plant in Martinsville, Virginia [1]. The overall results were highly favorable in demonstrating Coolside SO₂ abatement technologies. The pilot ESP showed excellent performance throughout the tests, with particulate removals approaching the theoretical maximum of the unit. With flue gas humidification at 20-25°F (11-14 K) approach to adiabatic saturation and additive (NaOH) injection at 0.1 NaOH/Ca(OH)₂ by weight, the observed SO₂ removals ranged up to 80% at sorbent utilizations of 35-40% in the Coolside configuration. During BLI activation testing at a 2.5/1 Ca/S mol ratio, the overall SO₂ removal increased from 50% without humidification to 65% with humidification at 25-30°F (14-17 K) approach to saturation. When additive (NaOH) was injected with the humidification water, the overall SO₂ removal approached 80%. Because these processes are in an early stage of development, we believe significant improvements are possible in increased SO₂ capture and reduced sorbent requirements.

PILOT UNIT

The pilot test unit was designed to simulate flue gas humidification. The unit is capable of matching actual flue gas conditions, such as temperature, gas composition, solids loading, and residence time, downstream of the air preheater in a coal-fired boiler unit.

Figure 3 is a schematic diagram of the Coolside pilot unit. The test equipment includes a natural gas combustor, ash and lime feeders, humidifier/reactor, humidification water/additive injection system, bag filter, water condenser and separator, and gas recycle blower. Of these, only the lime and additive feed systems and humidifier would be the components of an actual Coolside unit in a coal-fired power plant.

Simulated flue gas feed is produced by mixing the combustion products from the natural gas combustor, bottled

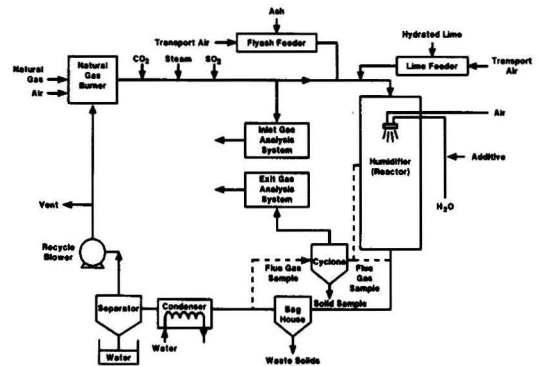


Figure 3. Schematic diagram of pilot unit.

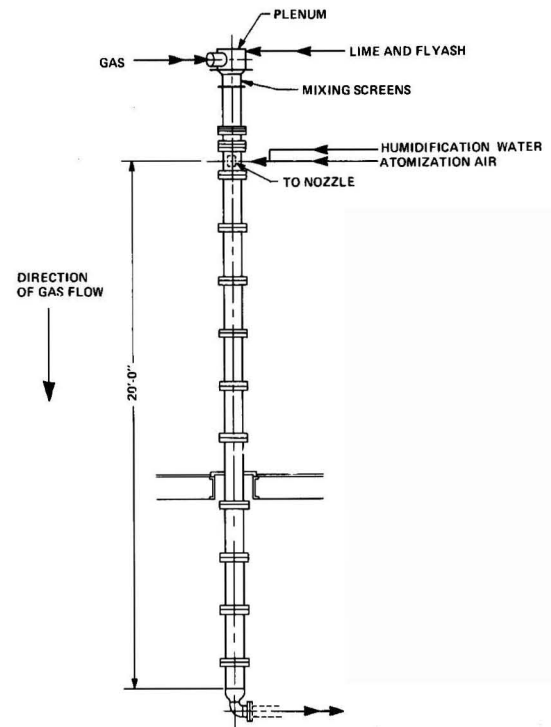


Figure 4. Reactor/humidifier design.

gases (SO₂ and CO₂), steam, and coal fly ash with a recycle stream from the process. The recycle stream provides over 80% of the total flue gas flow. The gas combustor serves both to generate make-up flue gas and to raise the recycle flue gas temperature to the desired level. The reactor/humidifier inlet temperature can be varied within a range of 250-400°F (394-477 K), adequately covering the range of flue gas temperatures found in coal-fired boilers. CO₂ is added since natural gas combustion produces less CO₂ than does coal combustion. SO₂, steam, and coal fly ash are added to the flue gas in variable amounts to simulate flue gases from different coals. The baghouse and the condenser/separator remove solids and water, respectively, from the flue gas before recycling.

Figure 4 is a simplified drawing of the humidifier. The humidifier is constructed of flanged sections of sch. 10 (8.3-inch, 21 cm ID), 316 stainless steel pipe. The overall length of the humidifier is just over 24 feet (7.32 m). The inlet section at the top of the reactor consists of an enlargement of the 6-inch (15.2 cm) flue gas inlet line to a 12-inch (30.5 cm) diameter plenum. The plenum significantly reduces the flue gas velocity. This helps smooth out the rapid transition from vertical upflow to horizontal flow to vertical downflow required at the top of the reactor. Attaining an even gas velocity profile before the nozzle port is essential for proper operation of the unit. Solids (lime and ash) are injected into the plenum section of the reactor.

The nozzle port is located about four feet (1.2 m) downstream of the plenum. The space between the plenum and the nozzle section contains perforated plates for gas profile straightening and gas-solid mixing. The nozzle section is followed by ten flanged pipe sections which provide a 20-foot (6.1 m) long humidification zone. These sections are equipped with ports for insertion of a borescope and fiber optic illuminators for viewing reactor internals. These allow observation of reactor flow patterns and inspection for solids deposition.

The baghouse is a nine bag unit with a total cloth area of 115 ft² (10.7 m²), giving a maximum air/cloth ratio of 4.1 acfm/ft² (0.021 m/s) at 150°F (339 K). The baghouse is heat traced and insulated to allow operation at the same approach to saturation as the humidifier. The unit is installed with two sets of SO₂ and O₂ gas analysis systems to measure the SO₂ removal data.

NOZZLE SPRAY DRYING TIME TESTS

Table 1 lists the results of drying time tests for several commercial nozzles. It shows a wide variation in drying times (0.5 to greater than 2.0 seconds) that is indicative of the wide variation in droplet size distributions produced by these nozzles. Table 1 also shows that, in general, higher atomizing air throughput and pressure gave shorter drying times for any given nozzle. The spray dry-

TABLE 1. DRYING TIME TEST RESULTS

Nozzle Operating Conditions

Nozzle	Air Pressure psig	Air Flow Rate scfm	Water Flow Rate gpm	Flue Gas Flow Rate scfm	Drying Time sec
Caldyne 2 mm	40	3.0	0.058	177	1.8-2.0
	50	3.5	0.058	178	1.6-2.0
	60	4.2	0.059	179	0.9-1.1
	80	5.5	0.055	177	0.6-0.9
FloSonic CN-2	30	6.59	0.082	300	1.2
	30	6.48	0.055	175	1.4-1.6
	50	9.30	0.092	300	1.2
	50	9.28	0.056	175	1.2-1.4
Bete HI-300	60	1.53	0.048	300	1.2
	60	1.32	0.055	175	2.0
	80	1.61	0.070	300	1.2
	80	1.80	0.053	175	2.0
Delavan SL	60	3.83	0.088	300	1.2
	60	3.84	0.055	175	2.0
	80	4.78	0.088	300	1.2
	80	4.78	0.058	175	1.6-1.8
Heat Systems Sonimist 700-3	40	10.2	0.065	175	1.0-1.2
	57	12.0	0.12	300	0.8-1.0
B&W Y-Jet	53	3.33	0.11	300	0.8-1.0
	92	6.20	0.13	300	0.8-1.0
Sonic Development St-47	23	3.25	0.11	335	1.0-1.2
	66	7.17	0.12	300	1.0-1.2
Spraying Systems J-12	115	3.3	0.058	175	0.7-1.0
	100	2.9	0.060	175	0.9-1.1
	90	2.3	0.072	200	1.1-1.3
	96	2.9	0.085	240	1.1-1.3
	70	2.1	0.057	175	1.4-1.8
	55	1.7	0.057	175	1.8-2.0

Common Conditions:

Inlet flue gas temperature: 300-330°F (422-439 K)

Approach to adiabatic saturation temperature: 20-30°F (11-17 K)

(1 psig = 6.894 kPa, 1 scfm = 0.02832 std m³/min, 1 gpm = 3.785 L/min)

Humidifier Gas Temperature, °F

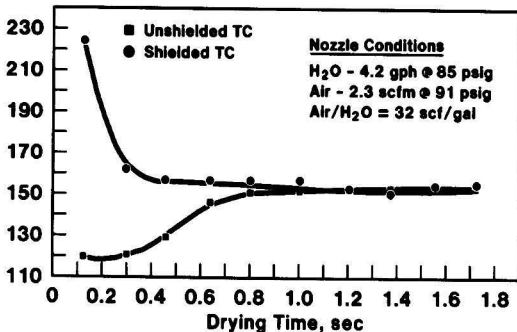


Figure 5. Pilot unit drying time test. Spraying Systems J-12 nozzle, 30°F (17 K) approach, flue gas inlet 300°F (422 K) and 200 scfm (5.66 std m³/min). (°F = 1.8 K - 460).

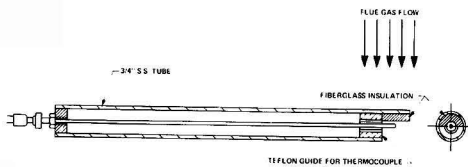


Figure 6. Shielded thermocouple assembly.

ing time is determined from temperature profiles measured by unshielded and shielded thermocouples along the axis of the humidifier. A typical profile is shown in Figure 5. The unshielded thermocouple reads the wet bulb temperature in the presence of liquid droplets due to the evaporative cooling of the droplets that impact the thermocouple. The shielded thermocouple, protected from droplet impingement (Figure 6) reads the gas phase (dry bulb) temperature. The drying time is obtained from the axial position at which the two thermocouples agree within thermocouple accuracy (2-3°F, 1-2 K) and/or the

point at which the unshielded thermocouple readings became constant.

Visual inspection of the internal wall of the humidifier showed a varying degree of wall wetting for most nozzles. The wall outer skin thermocouples read the wet bulb temperature at the wet spots. No wall wetting was observed for the Spraying Systems J-12 nozzle. The nozzles tested for drying time were chosen to have plume diameters of 10 inches (25 cm) or less at one foot (0.3 m) away from the nozzle, based on visual observations in a static test stand. This constraint was used to avoid any severe wall wetting that may occur with a nozzle having too large a spray plume. It was assumed that a plume of 10 inches (25 cm) under the static conditions would collapse to a plume of 8 inches (20 cm) or less under hot, flowing conditions in the humidifier. The observed wall wetting in the drying time tests indicate that the plume dimension may still have been too large for some nozzles to fit into the 8.3-inch (21 cm) ID humidifier.

DESULFURIZATION PERFORMANCE TESTS

Effect of Process Variables on SO₂ Removal

Table 2 shows the SO₂ removal and sorbent utilization data observed in pilot unit process variable tests. The primary objective, which was the demonstration of the reliability and reproducibility of SO₂ removal data, was achieved as discussed in a later section of this report. Table 2 also shows data from the 1 MW field tests [1] for comparison. The SO₂ removal levels and the observed variable effects from the pilot unit were reasonably consistent with the field data, although the pilot unit had a baghouse instead of the ESP of the field tests. The two test units used different atomization nozzles; Spraying Systems J-12 nozzle for the pilot unit, and Heat Systems 1100-1 for the field unit. In general, the SO₂ removal across the pilot humidifier and baghouse exceeded that across the humidifier and ESP in the field tests, an expected result since a baghouse provides better gas/solid contact.

In the pilot variable tests (Table 2) Runs 1 through 8 represented a two-level factorial experimental design using three key variables: the Ca/S molar feed ratio (1 and 2), the NaOH/Ca(OH)₂ additive mass ratio (0 and 0.1), and

TABLE 2. PILOT PLANT RESULTS (A)

Run	Process Variables			SO ₂ Removal, %		Baghouse Sorbent Utilization (b)		SO ₂ Removal % Across Humidifier + ESP in 1 MW Field Tests
	Approach °F	Ca/S mol Ratio	NaOH/Ca(OH) ₂ mass Ratio	Humidifier Only	Humidifier + Baghouse	Continuous Flue Gas Analyzers	Baghouse Hopper Ash Analyses	
1	48	1.0	0	13	18	18	20	12
2	48	1.0	0.11	21	27	25	26	20
3	48	2.2	0	22	29	13	17	26
4	48	2.0	0.10	43	48	22	25	42
5	23	1.1	0	31	38	35	36	26
6	23	1.0	0.11	38	48	44	40	45
7	23	2.0	0	34	50	25	25	42
8	24	2.1	0.11	60	85	37	37	75
9	24	1.6	0	30	44	28	24	—
10	25	0.6	0	12	20	33	34	—
11	29	1.0	0	17	29	29	26	—
12	28	1.9	0	29	44	23	23	—

(a) Common flue gas conditions: 300°F (422 K) inlet temperature, 122-126°F (323-325 K) adiabatic saturation temperature, 1.7-2.0 second humidification residence time and 1500 ppm (dry) SO₂ content.

(b) Both Ca(OH)₂ and NaOH are considered SO₂ sorbents with products being CaSO₃, CaSO₄, Na₂SO₃, Na₂SO₄.

(1°F approach = 0.5555 K approach)

TABLE 3. CHEMICAL AND PHYSICAL ANALYSES OF DRAVO LONGVIEW HYDRATED LIME (A)

Chemical Analyses, wt %	
Moisture	0.21
Ash	75.59
Carbonate	1.75
Ash Elemental, wt %	
Na ₂ O	0.01
K ₂ O	0.02
CaO	97.42
MgO	2.25
Fe ₂ O ₃	0.10
TiO ₂	0.02
P ₂ O ₅	0.01
SiO ₂	0.54
Al ₂ O ₃	0.57
SO ₃	0.07
Total	101.01
Particle Size Analysis, wt %	
+325 mesh (>44 microns)	21.6
-325 mesh (<44 microns)	78.4
BET Analyses	
Surface Area, m ² /g	17.3-20.3

(a) Typical analysis of batch used in pilot testing.

the approach to adiabatic saturation at the humidifier exit (25 and 48°F or 15 and 27 K). Runs 9-12 were conducted to further define variable effects. The J-12 nozzle was operated with an average atomizing air consumption of about 50 scf/gal (0.37 std m³/L) H₂O at 100 psig (689 kPa) atomizing air pressure, giving a drying time of 1-1.2 second at 25-30°F (14-17 K) approach (ca. 0.6 second at 45°F (27 K) approach). The total humidifier plug-flow residence time was 1.7-2.0 second in these runs. Humidifier inlet temperature was 300°F (422 K). The inlet SO₂ content was 1500 ppm. The feed hydrated lime was a typical high calcium lime (Table 3) obtained from the Dravo Longview plant. The lime had 17-20 m²/g surface area, somewhat lower than 22-24 m²/g of the lime used in the field tests. In all the runs, the feed lime was injected into the flue gas upstream of the water spray nozzle (Figure 3).

Effect of Ca/S mol Ratio

Figure 7 shows that the SO₂ removal increased with increasing Ca/S ratio over a range of 0.6 to 2.0, as expected based on field test results. The total SO₂ removal (humidi-

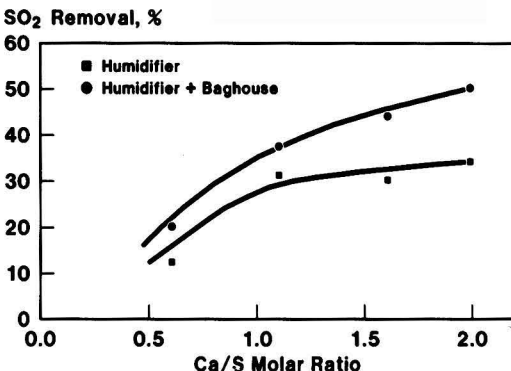


Figure 7. Ca/S ratio effect on desulfurization. 25°F (14 K) approach, no additive.

Humidifier SO₂ Removal, %

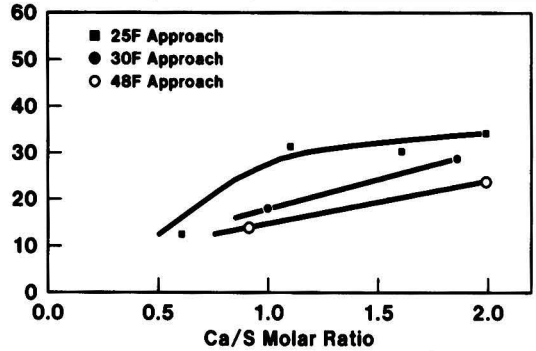


Figure 8. Effect of approach to adiabatic saturation on desulfurization in the humidifier. No additive. 1°F approach = 0.5555 K approach.

% SO₂ Removal Across Humidifier And Baghouse

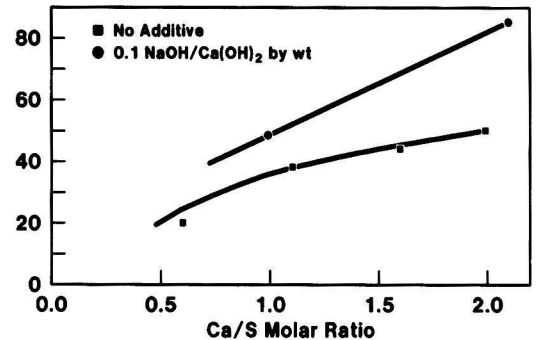


Figure 9. Additive (NaOH) effect on desulfurization. 25°F (14 K) approach.

fier + baghouse) increased from 20% to 50%, as the Ca/S ratio was increased from 0.6 to 2.0 at 25°F (14 K) approach with no NaOH addition. The SO₂ removal across only the humidifier increased from 12% at a 0.6/1 Ca/S ratio to 31% at a 1.1/1 Ca/S ratio and to 34% at a 2/1 Ca/S ratio at 25°F (14 K) approach and no additive. The humidifier SO₂ removal increase was not sensitive to increasing Ca/S ratios from 1.1 to 2.0. With the NaOH addition at 0.1 NaOH/Ca(OH)₂ by mass, the humidifier SO₂ removal was more sensitive to Ca/S ratio, increasing from 38% at 1/1 Ca/S to 60% at 2/1 Ca/S.

In general, the sorbent utilization efficiency decreased somewhat with increasing Ca/S ratio (Table 2), indicating a diminished incremental effect of additional sorbent feed. The sorbent utilization across the humidifier and baghouse at 25°F (14 K) approach with no NaOH dropped from 32% to 26% with an increase in the Ca/S ratio from 1.0 to 2.0. The sorbent utilization (U) was defined as

$$U = \frac{100 \Delta SO_2}{C + N/2} \quad (1)$$

where,
 ΔSO_2 = mol/hr SO₂ removed from the flue gas
 C = mol/hr Ca(OH)₂ fed
 N = mol/hr NaOH fed
 This assumes that SO₂ is captured as CaSO₄, CaSO₃, Na₂SO₃ and Na₂SO₄.

Effect of Approach to Adiabatic Saturation

The pilot test data showed that SO₂ removal significantly increased with closer approach to the adiabatic saturation temperature, as observed in the field tests. Figure 8 shows that at a 2/1 Ca/S ratio with no additive (NaOH), the humidifier SO₂ removal increased from 22% to 29% to 34% as the approach was lowered from 48 to 28 to 23°F (27 to 16 to 13 K). At the same conditions, the total (humidifier + baghouse) removal increased from 29% to 44% to 50%. These results indicate that both the humidifier SO₂ reduction and the reduction across the baghouse are sensitive to the approach to saturation. The increased capture in the humidifier may have been, in part, a result of the increased water feed required to achieve the lower humidifier exit temperatures. The theoretical water requirements for cooling to 48, 28 and 23°F (27, 16 and 13 K) approaches in the above runs were 0.288, 0.329, and 0.354 gal/1000 scf (0.0385, 0.0440 and 0.0473 L/std m³) flue gas, respectively. Liquid water droplets play a major role in sulfur capture during humidification, as discussed below.

Effect of NaOH Additive

As in the 1 MW field tests, NaOH injected with the humidification water significantly enhanced the Coolside SO₂ removal and sorbent utilization. The NaOH evidently acted both as an SO₂ sorbent and as a promoter for Ca(OH)₂. Figure 9 shows that the total SO₂ removal (humidifier + baghouse) at 23-25°F (13-14 K) approach and a 2/1 Ca/S ratio increased from 50% with no additive to 85% with the additive at 0.1 NaOH/Ca(OH)₂ by mass (0.185 by mol). This increased capture resulted in an increase in the sorbent (Ca and Na) utilization from 26% to 39%. The NaOH injection enhanced SO₂ removal both in the humidifier and in the baghouse. The humidifier SO₂ removal at the same conditions increased from 34% to 60% with the additive injection (0.1 NaOH/Ca(OH)₂).

The increased SO₂ removal with the NaOH injection was significantly greater than the stoichiometric amount of SO₂ absorbed by the injected NaOH in the form of Na₂SO₃ or Na₂SO₄ (Table 4). At a 1/1 Ca/S ratio and 23°F (13 K) approach, the increased SO₂ removal was 1.3 times the stoichiometric pickup. At a 2/1 Ca/S mol ratio, the increased SO₂ removal was 1.6 times the stoichiometric SO₂ pickup. These results indicate that NaOH and its reaction products (Na₂SO₃, Na₂SO₄) may promote the SO₂ capture by Ca(OH)₂. A similar effect was observed in the 1 MW field tests [1].

Sodium hydroxide injection also enhanced the SO₂ capture at higher temperatures. However, the absolute increases in SO₂ removal were not as great. At a 48°F (27 K) approach, the total SO₂ removal at 2/1 Ca/S increased from 29% to 48% with additive addition of 0.1 NaOH/Ca(OH)₂ by weight. This observed increase was about the same as the stoichiometric pickup by NaOH (Table 4).

Humidifier SO₂ Removal, %

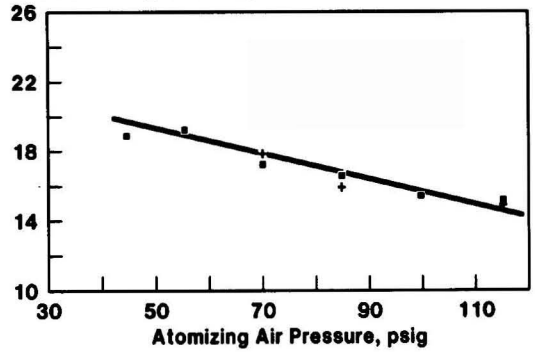


Figure 10. Effect of atomizing air pressure on desulfurization. Spraying Systems J-12 nozzle, 45°F (25 K) approach, 1.5 Ca/S molar ratio. 1 psig = 6.894 kPa.

Sodium hydroxide was used as the additive in the initial pilot testing, since this was the additive used in the 1 MW field tests. In our laboratory tests [2], other sodium based additives such as Na₂CO₃ and NaCl were equally effective in promoting sulfur capture. Future pilot tests will verify the additive effects of these compounds.

EFFECT OF WATER DROPLETS ON SO₂ REMOVAL

Based on pilot unit data, liquid water droplets play an important role in SO₂ capture in the humidifier. Two types of tests were conducted in the pilot unit to determine the effect of the water droplets on humidifier SO₂ removal.

First, flue gas was prehumidified with steam upstream of the lime injection point, thus producing a dry, humidified environment (no liquid droplets) for sorbent-SO₂ reactions. Second, a sorbent-laden flue gas was humidified by spraying liquid water and the atomizing air pressure was varied. The variation in the atomizing air pressure provided a variation in the droplet drying time in the humidifier.

The steam prehumidification tests showed that hydrated lime could remove some SO₂ under the dry, humidified conditions in the short contact time humidifier, but the level of SO₂ removal was significantly lower than that with water sprays in the humidifier. For these dry tests, steam was injected upstream of the lime injection point to expose the lime to a 150°F (339 K) simulated flue gas having a humidity level equivalent to a 25°F (14 K) approach to saturation. This produced a flue gas identical to that after complete droplet evaporation in a 25°F (14 K) approach Coolside process run. In this prehumidification test at the 25°F (14 K) approach, the humidifier SO₂ re-

TABLE 4. NaOH ADDITIVE EFFECT

Approach	Ca/S	Total % SO ₂ Removal (Humidifier + Baghouse)		Stoichiometric Utilization of NaOH (a)
		No Additive	0.10-0.11 wt of Ca(OH) ₂	
48	1.0	18	27	88%
48	2.0-2.0	29	48	117%
23	1.0-1.1	38	48	132%
24	2.0-2.1	50	85	152%

(a) Based on incremental SO₂ pickup between runs with and without NaOH injection and assuming conversion of NaOH to Na₂SO₃ and Na₂SO₄.

removal at a 1/1 Ca/S mol ratio was about 10%, which was much lower than 31% observed in a comparable Coolside run. The flue gas sorbent contact time was about 2 seconds in the prehumidification run. This result clearly indicates that water droplets and sorbent particles should be present together to maximize SO₂ removal in the humidifier.

Figure 10 shows that varying the atomizing air pressure using a J-12 nozzle changed the level of SO₂ removal observed at a 1.5/1 Ca/S mol ratio, no additive, and 45°F (25 K) approach to adiabatic saturation. The range of atomizing air pressure was 45-115 psig (310-790 kPa) in the test. The drying times measured for the 45°F (25 K) approach test were 0.5 and 1.2 seconds at 115 and 55 psig (790 and 380 kPa) air pressures, respectively. The differences in the drying time were due to differences in the water droplet size distributions, although the droplet size distribution was not experimentally measured. Figure 10 shows that, in general, larger droplets and longer drying times (i.e., lower atomizing air pressures) gave higher humidifier SO₂ removals. As the nozzle air pressure was decreased from 115 psig to 55 psig (790 kPa to 380 kPa), the humidifier SO₂ removal increased from 15% to 20%. However, a further reduction in the atomizing air pressure to 45 psi (310 kPa) reduced the observed SO₂ removal slightly. To better study the effect of droplet size

and drying time on humidifier SO₂ removal, additional pilot unit tests will be made using different nozzles and various nozzle operating conditions.

PILOT TEST OPERATION AND DATA RELIABILITY

SO₂ Removal Measurement

Reported SO₂ removals were based on flue gas SO₂ and O₂ contents measured by two (upstream and downstream) continuous flue gas sampling/analysis trains. Oxygen was measured using a Combustion Engineering Model 305A Analyzer to correct for air addition or leakage. The SO₂ analyzers were Thermoelectron Model 40 Pulsed Fluorescent Analyzer. The removal was averaged by a computer for 12-30 minute periods. Measured SO₂ removal was steady during the entire period of a run and was reproducible in repeat runs.

Two independent sampling methods were used for the flue gas between the humidifier and baghouse in order to prevent further SO₂ removal by the sorbent contained in the sample flue gas stream to the analyzer train: a cyclone sample system and a low-velocity sampling probe. The cyclone rapidly removed solids from the sample gas stream. The sample probe took a very small, low velocity stream flowing counter-current to the main flow. Because

TABLE 5. MATERIAL BALANCE RESULTS

Run	Total Solid Material Balance, % (a)			Elemental Material Balance, %		
	Baghouse	Humidifier deposits	Total (b)	Ca	Na	S
1	85.0	9.6	94.6	73.8	—	98.1
2	95.8	7.3	103.1	98.4	97.3	102.6
3	91.5	11.5	103.0	91.6	—	115.3
4	91.1	11.0	102.1	98.2	79.4	104.5
5	92.0	5.7	97.7	85.5	—	95.8
6	95.0	5.7	100.7	97.9	—	97.2
7	89.6	3.8	93.4	89.3	98.9	94.1
8	96.5	2.8	99.3	90.3	81.1	89.1
9	92.6	13.6	106.2	99.1	—	95.3
10	93.5	9.1	102.6	94.1	—	99.8
11	88.8	5.3	94.1	93.2	—	97.0
12	91.1	9.3	100.4	92.4	—	97.1

(a) Increase in solid mass due to SO₂ pickup is added to calculated solid feed mass.

(b) Out/In × 100.

TABLE 6. COMPARISON OF MEASURED WATER FEED RATE WITH REQUIREMENT FOR HUMIDIFICATION

Run	H ₂ O Feed, gph	Calculated H ₂ O Requirement, gph	H ₂ O Feed/ H ₂ O Required × 100
1	3.43	3.46	99 (103) (a)
2	3.34	3.44	97 (97)
3	3.46	3.46	100 (97)
4	3.87	3.65	106 (95)
5	3.73	3.59	104 (104)
6	3.85	3.67	105 (105)
7	3.79	3.72	102 (103)
8	3.66	3.52	104 (103)
9	3.64	3.39	107 (105)
10	3.40	3.44	99 (100)
11	4.05	4.05	100 (101)
12	4.03	3.95	102 (100)

(a) In parentheses, the water balance before addition of lime, ash and SO₂.
(1 gph = 0.06306 L/min)

of the high momentum of the particles toward the main flow direction, this probe method minimized solid entrainment in the sample gas. Additionally, both sampling systems were heated to ca. 300°F (422 K) to minimize relative humidity and, thus, lime reactivity. The two sample methods gave consistent measurements of the humidifier SO₂ removal.

Confirmation of Sorbent Utilization Data

Table 2 shows that the sorbent utilizations based on the baghouse solids chemical analyses were in good agreement with those based on the gas analyzer data. This confirms the reliability of the SO₂ removal data discussed earlier. The sorbent utilizations by the two methods differ by 0-4% absolute. The sorbent utilizations determined by gas analysis were used in the desulfurization discussion because the baghouse solids analyses could not provide the SO₂ removal data in the humidifier. We believe that for the total (humidifier and baghouse) SO₂ removal, the baghouse solid analyses provided reliable information and, thus, independently confirmed the gas analysis data.

Material Balances

Table 5 shows that the twelve Coolside runs in Table 2 had good total solid and elemental material balances. The overall solid material balances ranged from 93 to 106%. The elemental calcium, sodium and sulfur balances were 86 to 99% (except for 74% in the first run), 79 to 99%, and 89-115%, respectively.

Table 6 compares the actual humidification water feed rate during a run to the theoretical humidification water requirement. The theoretical water requirement is based on the material and energy balance calculations around the pilot humidifier. For the 12 Coolside runs, the measured feed rates were 97-107% of corresponding theoretical water requirements. This range indicates that the humidifier operation was adiabatic and that flue gas flow, water flow, and process temperature were accurately measured.

For a typical run, the pilot unit was first allowed to reach steady state operation with humidification only (i.e., no lime or fly ash feeds). The unit was run at steady conditions for at least an hour, during which time the drying time was measured and the nozzle and humidifier were inspected for any operating problems (e.g., wet walls). When the inspection showed no wall wetting, SO₂ was fed to the unit and, subsequently, fly ash and lime were fed. A material balance for the run took two to four hours. At the end of the balance, the SO₂, lime and ash feeds were terminated simultaneously. The humidifier was then inspected visually, using a borescope, for any wall deposition. Solids were quantitatively removed from the baghouse and the humidifier walls for a complete material balance. These solids samples were analyzed for sulfur, calcium, carbon, and moisture.

Humidifier Operability: Wall Solids Deposition

Table 5 shows that the mass of humidifier wall deposits collected after a run ranged 3-13% of the total solids throughput. Typically, this amount of solids from the wall

deposition represented a dry surface dusting with a maximum thickness of 1/16-inch to 1/8-inch layer (1 to 3 mm). This deposition created no serious operating problems and was removed by lancing with compressed air. Further, with a relatively small fraction of the total solids deposited, the deposition did not significantly distort measured SO₂ removals. This good humidifier operation with minimal wall deposition for these runs resulted from the run start-up procedures which ensured no wall wetting, as described above.

In some earlier runs (not reported here) with poor spray nozzle operation, humidifier wall deposition was more severe and adversely affected pilot unit operability. Severe humidifier deposition nearly always occurred during periods of operation with wet walls. For example, in some runs the J-12 nozzle was misaligned in the duct so that the spray plume impacted one side of the humidifier. In such cases, deposits formed quickly to a severe level, amounting to as much as 30-50% of the total solids throughput.

CONCLUSIONS

The pilot variable tests were successful in demonstrating the unit operability and data reliability. The levels of SO₂ removal and the effects of process variables (Ca/S ratio, additive (NaOH) rate, approach to adiabatic saturation) were consistent with those observed in 1 MW field tests made on a slipstream from an industrial boiler. These favorable results provide a firm base for future process improvement and optimization work using the pilot unit. Listed below are important results from the initial pilot work.

- Humidifier wall wetting and solids deposition can be minimized by selecting a nozzle having a spray plume size suitable for the humidifier internal dimension. For the 8.3-inch (21 cm) ID pilot humidifier, the Spraying Systems J-12 nozzle was operable without wall wetting.
- Hydrated lime injected into a dry, humidified flue gas gave a significant SO₂ capture. However, the presence of water droplets in the humidifier increased SO₂ capture significantly at the same level of humidification.
- The humidifier SO₂ removal may be significantly increased by operating the nozzle to produce droplets having an optimum size distribution. The SO₂ removal was generally higher at a lower atomizing air pressure using the J-12 nozzle. The drying time was longer at the lower atomizing air pressure.

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Treatment of a Water-Reactive Powder

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The treatment of water-reactive solid waste chemicals which generate corrosive products poses unique problems of feeding and reactor design. These problems have been addressed on a bench-scale and the design of a unit suitable for hazardous waste has been developed. The water-reactive material used was powdered titanium trichloride which was reacted with water (and oxygen) to give titanium dioxide and hydrochloric acid. The acid was neutralized by an alkaline scrubbing media.

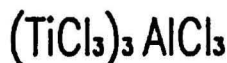
INTRODUCTION

The disposal of water reactive wastes is a continuing problem for both the waste generators and the waste disposal industry. It is frequently difficult, if not impossible, to find a disposal outlet for reactive materials such as titanium trichloride (Solid), titanium tetrachloride (Liquid), aluminum trichloride (Solid), silicon tetrachloride (Liquid), phosphorous pentasulfide (Solid), and other reactive materials. Usually these reactive waste materials are generated in fairly small quantities. Typical quantities from a single generator would be in the 25 to 250 kg per month range.

This paper describes the development of a treatment system for a specific solid reactive material; namely, aluminum-reduced titanium trichloride powder. The system developed can be used for other materials with only minor modifications.

MATERIAL PROPERTIES

Aluminum-reduced titanium trichloride has the formula $(\text{TiCl}_3)_3\text{AlCl}_3$ as shown in Table 1, giving an overall



$$\text{Ti} = 24.1\%$$

$$\text{Al} = 4.5\%$$

$$\text{Cl} = 71.4\%$$

Table 1. Aluminum-Reduced Titanium Trichloride

elemental composition as shown. The compound is a purple, free flowing powder with a density of 1200-1280 kg/m^3 . The compound is chemically stable when stored in drum containers under a dry nitrogen atmosphere. It has been safely stored in steel drums with a nitrogen blanket for periods in excess of 5 years.

Titanium trichloride hydrolyzes vigorously with water or moisture in the air, liberating hydrogen chloride and white oxides of titanium. The acid fumes liberated when water contacts titanium trichloride may cause a reaction with metals to release hydrogen gas, thus creating a fire hazard. Titanium trichloride is also a chemical reducing agent in the presence of oxidizers. When titanium trichloride is oxidized, sufficient heat may be liberated to cause a nearby combustible object to catch fire.

The commonly recognized injuries from titanium trichloride are thermal and acid burns caused by contact of the material with the skin or eyes in the presence of moisture. On contact with moisture, corrosive hydrogen chloride is produced. No acute systemic effects have been recognized. No form of chronic toxicity has been recognized, either systemic or local.

There are no established threshold limit values for titanium trichloride. However, the American Conference of Governmental Industrial Hygienists has assigned a threshold limit of 5 ppm (7 milligrams per cubic meter) in air as the maximum allowable concentration of hydrogen chloride vapor for exposures not exceeding a total of eight hours daily.

The odor and irritating properties of hydrogen chloride may serve as a warning of its presence in the air.

LABORATORY STUDIES

The laboratory study was initiated due to a request from a generator. This particular generator had developed an inventory of off-spec reactive material and was unable to find an acceptable disposal outlet.

The original sample of the aluminum-reduced titanium trichloride was received in a glass screw top bottle containing a little over 500 grams of material. In order to reduce the potential for a significant spill during the laboratory testing, it was decided to transfer the original sample into more manageable containers of 100 grams each. A sheet of heavy gauge clear plastic was taped to form an

envelope. The powder sample, several tared screw top glass bottles, and an assortment of spatulas were placed in the envelope. The bag was then taped shut except for a small vent. The bag was purged with nitrogen for two hours. The powder was then transferred to the smaller bottles in quantities of approximately 100 grams each. By displacing the moist air with nitrogen, no reaction took place during the transfer. The bottles were reweighed to determine the net weight of the powder. The entire operation took place in a laboratory hood as an added safety precaution. The samples were then stored until the laboratory reactor was ready.

A small laboratory reactor was constructed as shown in Figure 1. The main body of the reactor was made of clear acrylic plastic since it is easy to machine and would allow observation of the reaction. Two fan-pattern spray nozzles were constructed from copper tubing. These nozzles produced a flat spray pattern in the horizontal plane, with a cone angle of about 90°. The nozzles were offset 180° with a one inch difference in elevation. At a flow rate of approximately 3.7 liters/minute the 2 sprays gave almost 100% coverage of the reactor I.D. Standard PVC socket type pipe reducing fittings were used for the end pieces.

The top fitting had a plastic powder funnel cemented into it for addition of the material to be reacted. Two 0.64 cm vents were also installed in the top fitting to prevent a vacuum buildup in the reactor in case the material should block the entrance to the reactor.

The bottom fitting was reduced to accommodate 1.27 cm rubber tubing which drained into a 55 liter plastic open top tank. A pinch clamp was used on the tubing to control the drain rate so as to maintain 5.0 to 7.5 cm of liquid in the bottom of the reactor.

A 0.64 cm fitting was installed 10.2 cm above the bottom of the reactor tube and connected to a vacuum source through a 500 ml glass scrubber bottle (not shown). This was installed to collect any HCl gas that did not immediately go into solution, or any unknown reaction products

that may have formed due to contaminants in the material being reacted. The vacuum purge also reduced the potential of the feed material blowing back from the reactor in the event of a sudden gas release. The laboratory reactor system was set up in a walk-in hood as an added safety precaution.

At the start of each test, the vacuum airflow through the reactor was set at 30 liters/minute (~1 CFM). The exhaust was routed through a 500 ml glass scrubber bottle containing 1.0 normal sodium hydroxide. The scrubber was provided to determine the efficiency of the reactor and to protect the vacuum system in case any HCl gas escaped from the reactor. The water sprays were then adjusted to a total flow of approximately 3.7 liters/minute (~1 GPM). The pinch clamp on the discharge hose was adjusted to produce a constant 5.0 to 7.5 cm of liquid in the bottom of the reactor. This usually required appropriately 30 seconds. A 100 gram sample of aluminum reduced titanium trichloride was then manually added to the top of the reactor. The addition rate was somewhat variable, but in each test 85 to 105 grams of aluminum-reduced titanium trichloride were added over a 4 minute, plus or minus 20 seconds, time period. As soon as the cap was removed from the 100 gram sample bottle a white "smoke" was visible. During the feed addition period the reactor was filled with the white "smoke", but none escaped out the feed end. The water sprays and vacuum were allowed to operate for 30 seconds after the last of the powder was added. Runs were performed with and without caustic in the bottom sump. After each run the acidity or the alkalinity of the bottom sump and the scrubber, along with the amount of suspended solids were determined. These data were then used to perform a mass balance.

The laboratory runs held no surprises and were somewhat anticlimactic after all the preparations.

REACTION CHEMISTRY AND LABORATORY RESULTS

Water Reactivity

Titanium trichloride is known to react vigorously with water according to Equation 1 shown in Table 2 and below.



The product, Ti_2O_3 is titanium sesquioxide, a purplish-black, water insoluble precipitate. Titanium sesquioxide is stable in the absence of oxygen; however, it is readily oxidized by oxidizing agents or exposure to atmospheric oxygen as shown in Equation (2).

Table 2. Reaction Chemistry

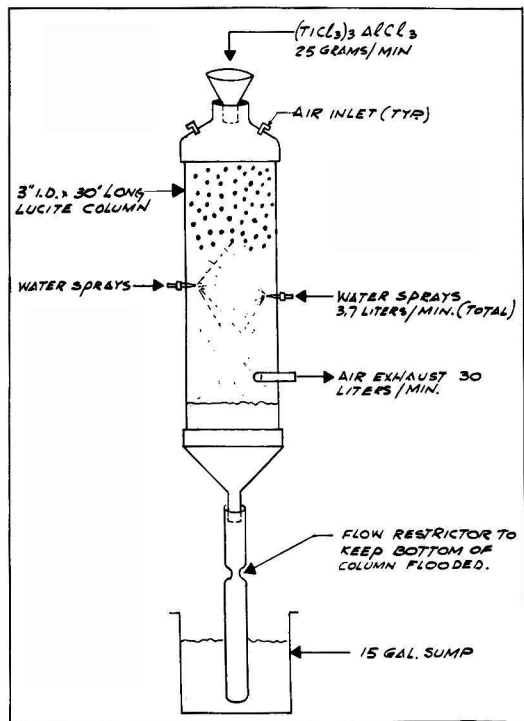
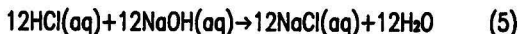
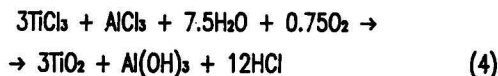
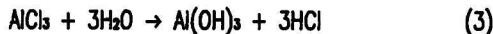


Figure 1. Laboratory Reactor

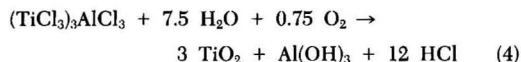


This product, TiO_2 is titanium dioxide, a stable, non-toxic, white precipitate. Because of these properties and its high refractive index and lack of absorption of visible light, it has become the predominant white pigment in the paint industry.

Anhydrous aluminum chloride is also highly water reactive, liberating hydrogen chloride as shown in Equation (3).

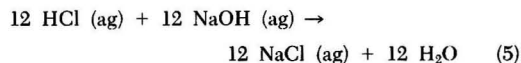


Reactions (1) and (3) are somewhat simplified in that the formation of the hydrolysis products is pH dependent due to the stepwise formation of oxides and hydroxides, however, at neutral to mildly basic conditions the products are primarily Ti_2O_3 and $\text{Al}(\text{OH})_3$. The overall reaction of aluminum reduced titanium trichloride with water, followed by oxidation of the titanium sesquioxide is shown in Equation (4).



Neutralization and Precipitation

As shown in Equation (4), 12 moles of HCl will be formed. If the HCl formed is neutralized using NaOH, 12 moles of NaCl and 12 moles of water will be produced as shown in Equation (5).



The hydrolysis products formed in the reaction of aluminum reduced titanium trichloride with water are somewhat soluble at the low pH of approximately 1.5 that results if no caustic is added to the system. Without the addition of caustic, the suspended solids are only about 13% of the total solids in the reaction products.

As the pH is raised to between 3-4, a dark blue precipitate is formed, indicating the precipitation of Ti_2O_3 from other hydrolysis products soluble at low pH. At this pH the precipitate is extremely fine, and does not settle readily.

Raising the pH above 7, results in a dramatic increase in flocculation assisted by the formation of $\text{Al}(\text{OH})_3$ from its low pH hydrolysis products. At above neutral pH, sedimentation is extremely rapid.

Oxidation

At neutral or alkaline pH, the Ti_2O_3 floc is readily oxidized as indicated by the transition from a dark blue to a white floc. The stirred floc reacts immediately with sodium hypochlorite solution. The floc can also be readily oxidized in a few minutes by bubbling air through it. After oxidation and at a neutral or alkaline pH, the titanium dioxide and aluminum hydroxide floc settles rapidly.

Heat of Reaction

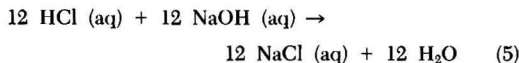
The heat of reaction plus the heat of dissolution of HCl for the overall hydrolysis reaction (reaction 4) is -263 KCal/mole of aluminum-reduced titanium trichloride or 1.849 kJ/kg of starting material. Assuming a flow rate through the reactor of 83.5 liters water per kg of reactant, the maximum temperature increase of the water can be calculated:

$$\frac{1.849 \text{ kJ} \times 1 \text{ kg reactant} \times 1.0 \text{ liter H}_2\text{O} \times 1 \text{ KCal}}{\text{kg reactant} \times 83.5 \text{ liters H}_2\text{O} \times 1.0 \text{ kg H}_2\text{O} \times 4.187 \text{ kJ}} = \frac{5.29 \text{ KCal}}{\text{kg H}_2\text{O}}$$

This corresponds to a maximum temperature increase of 5.3°C for the reactor water. Of course, this assumes the following:

- All the heat released is captured by the water, ignoring the heat removed by the gas flow from the vacuum purge.
- There is no heat exchange with the surroundings.
- Oxidation of Ti_2O_3 to TiO_2 takes place quantitatively in the reactor. (It does not, according to observations).

Another source of heat release is the heat of neutralization of the 12 moles of HCl generated by one mole of aluminum-reduced titanium trichloride as shown in Equation (5).



The heat of reaction for equation (5) is -162.8 KCal/mole of $(\text{TiCl}_3)_2\text{AlCl}_3$ or 1.144 kJ/kg of starting material. Again, assuming 83.5 liters of water per kg of reactant, this corresponds to a maximum temperature rise of 3.3°C.

Adding both heat releases, we see that a maximum temperature rise of 8.6°C can be expected, when 83.5 liters of water is used for each kg of feed. During the laboratory testing, the water to feed ratio was closer to 167 liters per kg. Although the temperatures were not closely monitored, the temperature rise was less than 3°C in all of the experiments.

Reaction Products

Per kg of feed material, the expected stoichiometric requirements of reactants, assuming sufficient caustic is added to neutralize the HCl formed, is:

REACTANTS

$(\text{TiCl}_3)_2\text{AlCl}_3$	= 1.00 kg
H_2O	= 0.23 kg
NaOH	= 0.80 kg

The resulting products, assuming complete oxidation would be:

RESULTING PRODUCTS

TiO_2	= 0.402 kg
$\text{Al}(\text{OH})_3$	= 0.131 kg
(This would produce 0.533 kg of suspended solids).	
HCl	= 0.734 kg

Neutralization of the HCl with NaOH will produce 1.176 kg of sodium chloride (NaCl). Assuming excess water is used, the NaCl will be in solution.

FULL SCALE PROCESS

Design

As a result of the laboratory testing, a full scale reactor system has been designed. A simplified flow diagram is shown in Figure 2. The system is designed specifically for aluminum-reduced titanium trichloride, but could be utilized for other reactive wastes with minor modification. Reactive wastes requiring disposal have a tendency to be of the "one-shot" nature. Frequently requests for disposal result from an upset in production or material that has been stockpiled for many years because no disposal outlet was available. For this reason, a reactor sys-

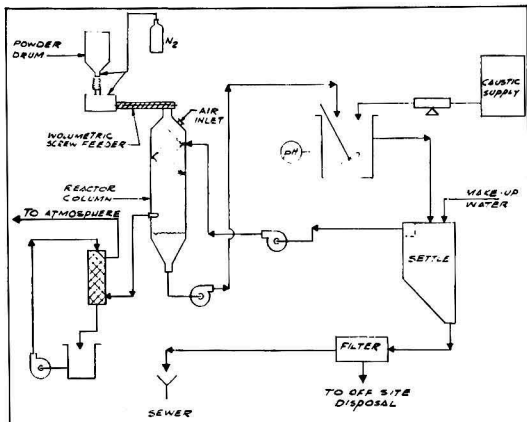


Figure 2. Reactive Chemical Treatment System

Table 3. Full Scale Treatment System Mass Balance (Not Including Scrubber System)

$(TiCl_3)_2 AlCl_3$	136 kg/Hr	WASTE WATER	$H_2O = 11,167$ kg/Hr	SEWER
		$NaCl = 159$ kg/Hr		
H_2O	11,349 kg/Hr	$N_2 = 34$ m ³ /Hr		ATMOSPHERE
$NaOH$	109 kg/Hr	FILTER CAKE	$TiO_2 = 54.9$	TO LANDFILL
N_2	34 m ³ /Hr		$Al(OH)_3 = 17.7$	
			$H_2O = 181.4$	
			$NaCl = 2.7$	
			TOTAL = 256.7 kg/Hr	

As an added safety precaution, a small caustic scrubber will be used to purge the reactor column. The reactor will be operated at a very slight negative pressure to reduce the possibility of any HCl gas escaping into the atmosphere.

Mass Balance

Table 3 presents a mass balance for the entire operation, except for the caustic scrubber operation. This drawing has been greatly simplified, and is used only to give an indication of the quantities of materials used and products produced in a commercial application. The mass balance assumes 83.5 liters of water is consumed for each kg of aluminum-reduced titanium trichloride fed to the reactor. No water recycle is included, whereas at least 50% water reuse should be possible if heat removal is included, and depending on the salt discharge limits of the POTW being used.

At 136 kg per hour, the system could treat 4 to 5 drums of material per 8 hour shift. At one shift per day, 80 to 100 drums per month could be processed. This may seem like a very small capacity for a commercial operation, but it is suitable for the available quantities of reactive waste requiring treatment.

In addition to the 136 kg per hour of titanium trichloride, 109 kg of sodium hydroxide, and 11,349 kg of water could be added (assuming no water recycle). The 34 cubic meters per hour of nitrogen gas is for purging the feed system of air and does not enter into the reaction.

The resulting 11,594 kg per hour of feed will result in a solid and a liquid stream for disposal. The liquid stream will be about 11,165 liters of water per hour that contains approximately 1.4 weight per cent salt. At the most, the temperature of this stream would be elevated 8.6°C.

The solids from the dewatering operation amount to approximately 257 kg per hour assuming 60% moisture. This material will be collected in drums or a roll-off box for disposal.

Conclusion

The laboratory testing indicates that a relatively unsophisticated system can be used to safely treat various industrial reactive powders. Reaction of the powder with water can be controlled and air emissions minimized with the aid of a wet scrubber. The acid water produced can be neutralized with sodium hydroxide producing a filterable solids floc. The dewatered solids can be disposed of in a landfill and the filtered water is suitable for discharge to the POTW in most cities.

tem should be adaptable to other types of reactive materials. The systems presented in this paper can be easily adapted to handled liquid wastes, as long as the materials of construction are suitable.

The system is designed around a 30.5 cm diameter, 3.05 cm long fiberglass reactor column. Other materials such as PVC pipe could be used, but PVC does not have the structural strength nor the heat tolerance of fiberglass. Metallic reactors should be avoided because of the corrosion from the HCl, and because of the potential for hydrogen generation. A maximum process rate of up to 136 kg per hour of aluminum-reduced titanium trichloride is anticipated.

The aluminum-reduced titanium trichloride is received in special, 53 gallon (200 liter) steel drums. The drums are pressurized to 34.5 kPa and contain approximately 180 kg of aluminum-reduced titanium trichloride. The drum is inverted and placed in a cradle using a small overhead crane. A 3 inch (7.6) cm pipe nipple is screwed into the drum flange, and connected to a flexible Teflon[®] bellows. The other end of the bellows is connected to the feed hopper of a variable speed volumetric screw feeder. The hopper is sealed and epoxy coated. The screw feeder auger is stainless steel and the discharge nozzle is Teflon[®]. A gaseous nitrogen supply (or -45°C dewpoint air) will be used to purge the valving arrangement (not shown) and screw feeder.

The screw feeder discharges the reactive powder into the top of the reactor column. The feed material drops through the water spray provided by 6 to 10 spray nozzles. The water (neutral to slightly alkaline) will be pumped at 190 liters per minute. The water and suspended solids will be pumped from the bottom of the reactor to a pH adjust tank where sodium hydroxide will be used to maintain the pH between 8 and 9. After the pH adjust the fluid will be transferred to a gravity settler. The bottoms will be dewatered using either a belt filter or a filter press. The clarified liquid will then be recirculated back to the reactor column after the addition of the necessary make up water is added. For the mass balance calculations presented in this paper it was assumed that the water is used once and discharged after removing the solids.

The dewatered solids (30-50% solids) will be transported to a secure landfill for disposal. The filtrate will be discharged to the POTW.

Evaluating Potential Impacts from Accidental Gaseous Releases of Toxic Chemicals

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Many companies involved with toxic gases are seeking an independent evaluation of liability in the event of an accidental release. A detailed methodology is presented with a hypothetical example based on case studies from several recent risk assessments. These demonstrate such typical components of an analysis as site reconnaissance, accident scenario development, air quality assessment, health impacts potential and remedial action review.

INTRODUCTION

Concern about risks and consequences of accidental releases of hazardous chemicals to the air has increased in recent years. To date, most attention has been focused on large chemical manufacturing facilities where vast amounts of potentially dangerous chemicals are produced, stored and transported. However, users of even relatively small amounts of toxic gases may have legitimate concerns about the risk of an accidental release. Possible reasons include: (1) limited training on the hazards of handling and using toxic gases, (2) potential worker exposure due to improper ventilation system design, (3) potential off-site exposure due to the close proximity of a source to the property boundary. This paper presents a methodology which has been applied to chemical user facilities to help evaluate the level of risk and to design appropriate mitigation measures.

The risk evaluation begins with an environmental audit which includes detailed interviews with plant personnel, on-site inspection of the facility and critical review of toxic gas storage, handling and transport procedures. A site inspection is sometimes the only way that possible safety environmental hazards can be detected. One-on-one interviews provide insight into the knowledge and safety consciousness of those who control the use of toxic gases. A risk assessment of potential consequences of an accidental release is typically comprised of several components: (1) identifying potentially hazardous gases, (2) determining both routine and possible accidental modes of release, (3) estimating release rates for selected cases, (4) locating potentially sensitive receptors, both on-site and off-site, (5) modeling dilution and transport from the source to each receptor, (6) relating resultant concentrations to potential adverse health effects and, (7) evaluating possible mitigation measures.

Each of these components are discussed in detail along with examples of impact assessment for a hypothetical facility that uses several hazardous gases stored under pressure. Application of this analysis process required information that is often distributed among several functional groups at a facility. These include health and safety, environmental, and plant operations engineering personnel. It is important to obtain the relevant contributions from

each to avoid missing important factual data. Even firms with environmental and safety staff often seek an independent risk assessment from an outside expert to lend credibility to the study and its recommendations.

GENERAL METHODOLOGY

Criteria for a site-specific risk assessment vary with both the type of facility and its setting. The on-site environmental and safety audit of the plant and its operations plays an integral part in establishing these criteria. The concerns of the facility's health and safety personnel usually provide the best starting point in conducting a site review. The first step is to obtain an inventory of toxic gases that are used or produced at the facility, along with any processes that routinely result in atmospheric emissions. Table 1 provides a checklist for this chemical inventory.

The next step is to identify the types of accidents that could lead to episodic releases. An effective way of doing this is to discuss experience with plant operations personnel and to review historical records for the plant and the industry at large. Table 2 provides samples of the types of accidents that may be considered in the risk assessment.

TABLE 1. HAZARDOUS CHEMICAL INVENTORY

Threshold Values for Acute Hazards	
—toxic	
—explosive	
—pyrophoric	
—carcinogenic	
Storage Conditions	
—pressurized gas	
—liquified gas	
—cryogenic liquid	
—volatile liquid or solution	
Type and Capacity of Storage Vessel	
—portable gas cylinders	
—above-ground tanks	
—below-ground tanks	
Location	
—delivery route	
—central storage	
—end use points	
—process emission points	

TABLE 2. TYPES OF ACCIDENTS THAT CAN RESULT IN HAZARDOUS AIR RELEASES

Storage	—fracture of a compressed gas valve —overheating of a gas cylinder —leakage from a worn or corroded valve —collision (<i>e.g.</i> , railcar) resulting in a vessel rupture
Process	—runaway reactions —failure of control device —leakage from gas supply line —other upset conditions
Catastrophic	—fire —explosion —severe weather events —earthquakes

In some instances, the probability of occurrence for each type of accident may be quantitatively evaluated, although those involving human error have an inherent degree of uncertainty. Formal analysis techniques available include criticality analysis, fault tree analysis, event tree analysis, case-consequence analysis and human error analysis [1]. Caution is required in using industry-wide statistics in estimating accident probabilities because they may not fairly represent the site-specific conditions. Therefore, in most instances the list of "worst-case" accidents to be analyzed in the risk assessment is determined subjectively. One practical way is to separate those accidents that are caused by external forces beyond the reasonable control of the facility and its personnel (*e.g.*, sabotage, earthquake, aircraft crash).

Once a set of potential accidents have been defined, the next step is to evaluate the resultant quantity and rate of release. For accidents involving volatile liquids or gases stored under pressure, the rate of release to the atmosphere depends on a variety of physical and thermodynamic properties such as those identified in Table 3 [2]. This data is used as input into specialized emissions models.

The next step is to determine the set of on-site locations at which each type of accidental release is possible and at which of these locations is the potential for on-site and off-site impacts the greatest. At some locations, such as a gas storage facility, several different chemicals may be at risk. It is useful to rank the gases according to acute health impact potential. One method is to compile a score for each chemical, such as the ratio of the initial maximum instantaneous air emission possible to an appropriate measure of the acute toxicity. The impact of the highest-ranked chemical then represents the greatest consequence for a particular release scenario.

Once the hypothetical release has been quantified the potential routes of exposure can be evaluated. The manner in which the chemical is released into the air can have a large effect on the rate of dilution and resultant concentrations. Table 4 provides examples of the various types of release behavior that may be encountered. It is, therefore, important to have the proper dispersion modeling tools to

TABLE 3. FACTORS INFLUENCING RELEASE RATE OF PRESSURIZED GASES

- Size, shape and composition of storage vessel
- Size and shape of leaking orifice
- Initial pressure, temperature and amount
- Liquefied or compressed gas
- Height of orifice with respect to liquid level
- Specific heats of liquid and vapor
- Densities of liquid and vapor
- Heat of vaporization
- Saturation vapor pressure
- Ambient temperature, wind speed, and humidity
- Compressibility
- Viscosity

TABLE 4. AIRBORNE RELEASES REQUIRING SPECIALIZED MODELING TECHNIQUES

- Time varying release
- Evaporation of volatile liquids and solutions
- Sonic jet flow emitted from a critical orifice
- Release of heavier-than-air gases (*i.e.*, higher molecular weight or lower temperature than ambient air)
- Flashing of a liquid aerosol spray forming a cold, dense cloud
- Evaporation of cryogenic pool of liquefied gas
- Release into the wake cavity zone of a building and entrainment of contaminated air into ventilation ducts
- Indoor release emitted to the atmosphere through the ventilation system
- Explosive release of pyrophoric or other highly reactive chemicals

effectively simulate various modes of atmospheric dispersion.

The principal consideration in the risk assessment is the receptor, *i.e.*, the location where potential human exposure would ultimately occur. The various possible locations for on-site and off-site receptors are shown in Table 5. The potential acute health impacts at each receptor and required safety factors can be evaluated according to health assessment criteria established for each chemical and the expected sensitivity of individuals who may be exposed. (For instance, an acute exposure that may not adversely affect a healthy adult may cause injury to a child.) Another problem that may be important in a health risk assessment is the simultaneous exposure to several toxic chemicals; that may have similar or dissimilar effects.

After the on-site and off-site consequences of episodic worst-case release scenarios have been evaluated, additional mitigation analyses may be warranted. These analyses quantify the reduction in risk associated with measures such as those listed in Table 6 which can be taken to reduce the worst-case emission, enhance the dispersion of the accidental release, or displace the most critical receptors.

RISK ASSESSMENT FOR CASE STUDY OF A TOXIC GAS STORAGE FACILITY

Site Survey

The subject facility contains pressurized cylinders of chlorine, anhydrous ammonia, and arsine (10%), all stored in ventilated cabinets which exhaust through to a roof vent. To identify locations for potential accidental release scenarios the transportation route of a cylinder is traced from the point at which the gas vendor enters plant property to the point of use. The most common cause of leakage from a pressurized gas cylinder is through damage to the valve assembly [3]. This can occur, for instance, if the safety cap is absent or not tightly secured and a cylinder falls during transport. A high pressure gas cylinder with a sheared valve can be propelled by such force from the escaping gas that it can penetrate masonry walls [3].

TABLE 5. TYPICAL LOCATIONS WHERE EXPOSURE TO AIRBORNE HAZARDS ARE EVALUATED

On-Site	Indoor	—in the vicinity of the accident —in adjacent offices and buildings
	Outdoor	—building air intake ports —pedestrian walkways —roadways and parking areas
Off-Site		—fence line or property boundary —closest residences —schools —hospitals —public areas (parks, malls) —industrial/commercial neighbors

TABLE 6. MITIGATION MEASURES FOR HAZARDOUS GASEOUS RELEASES

- Strictly enforce safe chemical handling procedures
- Reduce amount stored in a single vessel
- Design loading dock such that accidental emissions are vented to a stack rather than released at ground level
- Restrict on-site transport of toxic gases to avoid collision hazard
- Increase the height and flow rate of ventilation stacks to enhance dispersion
- Relocate fresh air intakes to reduce the potential for entrainment of contaminated air
- Install emergency scrubbers or ventilators
- Purchase abutting property.

Ventilation in the loading dock, corridors, chemical storage facility and laboratories, wherever the toxic gases are routed, is carefully reviewed. Documentation of air-flow in each storage or use area will help to determine the path that an accidental emission will take. If, for instance, an accident occurs outdoors on an exposed loading dock, emissions will be dispersed directly into the atmosphere. An accident in a corridor which shares recirculated air with other parts of the building could cause widespread indoor contamination. On the other hand, a release within a properly ventilated storage facility could be carried to the atmosphere via a rooftop stack, and perhaps through a control device.

Once the gas is released to the atmosphere it can be transported by the wind away from on-site receptors or become drawn into buildings through fresh air intake vents, thereby causing on-site contamination. The rate at which dilution occurs and the direction that the gas is likely to be transported in the atmosphere is a function of the meteorology in relation to the local building configuration. For most areas of the United States statistical information on wind speed and direction can be obtained from measurements taken at a nearby airport, if they are not available from onsite tower measurements. The dimensions and configuration of on-site buildings and representative meteorological data are then used in conjunction with source emissions, location, and venting characteristics to estimate concentrations at important receptors by means of an air quality dispersion model.

Accidental Emissions

As shown in the site map (Figure 1), two accidental release locations are considered, an outdoor release on the loading dock (A) and an indoor release vented through a rooftop stack (B). The map also shows locations of receptors where the impacts of accidental releases are evaluated. Receptors 1-7 are located along the property boundary, 8-12 at specific off-site locations, 13 at a fresh air intake and 14-15 at on-site parking and pedestrian walkways.

The first task was to determine which gas poses the greatest potential off-site health hazard in the event of

sudden release. The most important factors governing the emission release rate are the valve outlet diameter, initial cylinder pressure, temperature and, for liquified gases, saturation vapor pressure and cylinder orientation [2]. For a worst-case release a mechanical valve failure is assumed. The maximum possible size of the fissure in each valve can be determined from CGA (Compressed Gas Association) valve diagrams.

For purposes of ranking acute toxic gas releases, the Immediately Dangerous to Life or Health (IDLH) values defined by OSHA (Occupational Safety and Health Administration) are often used [4]. While the actual toxic impacts may depend on other factors not accounted for in the IDLH, this value serves as a useful benchmark. The score used in this example ranking is simply the amount in each cylinder divided by the IDLH. Table 7 shows that chlorine probably poses the greatest acute hazard for the storage containers utilized at this site.

Dispersion Modeling

Emissions from the two accident locations, the outdoor loading area and inside the ventilated building, are used in the dispersion model calculations. The loading dock release is often the more critical, because an accident would result in essentially a ground-level release, thereby maximizing surface impacts.

An Integrated Puff Dispersion Model (IPDM) can be used to obtain concentrations in the direct path of the release as a function of time and distance. The model accounts for the initial dimensions of the "cloud" of emissions, wind speed, and atmospheric stability. The initial dimensions of the release is a complex function of several factors including the momentum of the pressurized jet from the fractured valve, the gravitational spread of the dense cloud and the mixing caused by turbulence from the nearby building wake. For each gas, an analysis is performed to determine which effects dominate the initial volume of the cloud. In the loading dock release case, for example, the building wake effect, rather than dense gas dispersion may determine the initial size of the cloud, whereas "passive" dispersion dominates at distances beyond the building wake region. The plot of the chlorine concentration in Figure 2 shows how the concentrated puff of material can disperse rapidly with downwind distance.

To estimate peak short-term (e.g., one-minute) average, ground-level concentrations due to neutral or positively buoyant emissions from various sources (loading docks, stacks, roof vents) a modified version of the U.S. EPA's Industrial Source Complex (ISC) model can also be used. EPA's Industrial Source Complex (ISC) model can also be used. The utility of the ISC model is that it incorporates building downwash wake effects and plume rise and is the standard model used in regulatory applications for a wide variety of industrial sources. However, because the model is designed to simulate continuous releases, adjustments to the model calculations need to be made to

TABLE 7. HAZARD RANKING OF GASES FOR THE CASE STUDY

Rank	Chemical Name	Amount* (m ³)	IDLH (ppm)	Relative Hazard Score* (%)
1	Chlorine	2.15	25	100
2	Ammonia	17.95	500	42
3	Arsine	0.08	6	16

*Amount/IDLH (normalized to 100 for chlorine)

*Amount is the volume of substance at room temperature and ambient pressure.

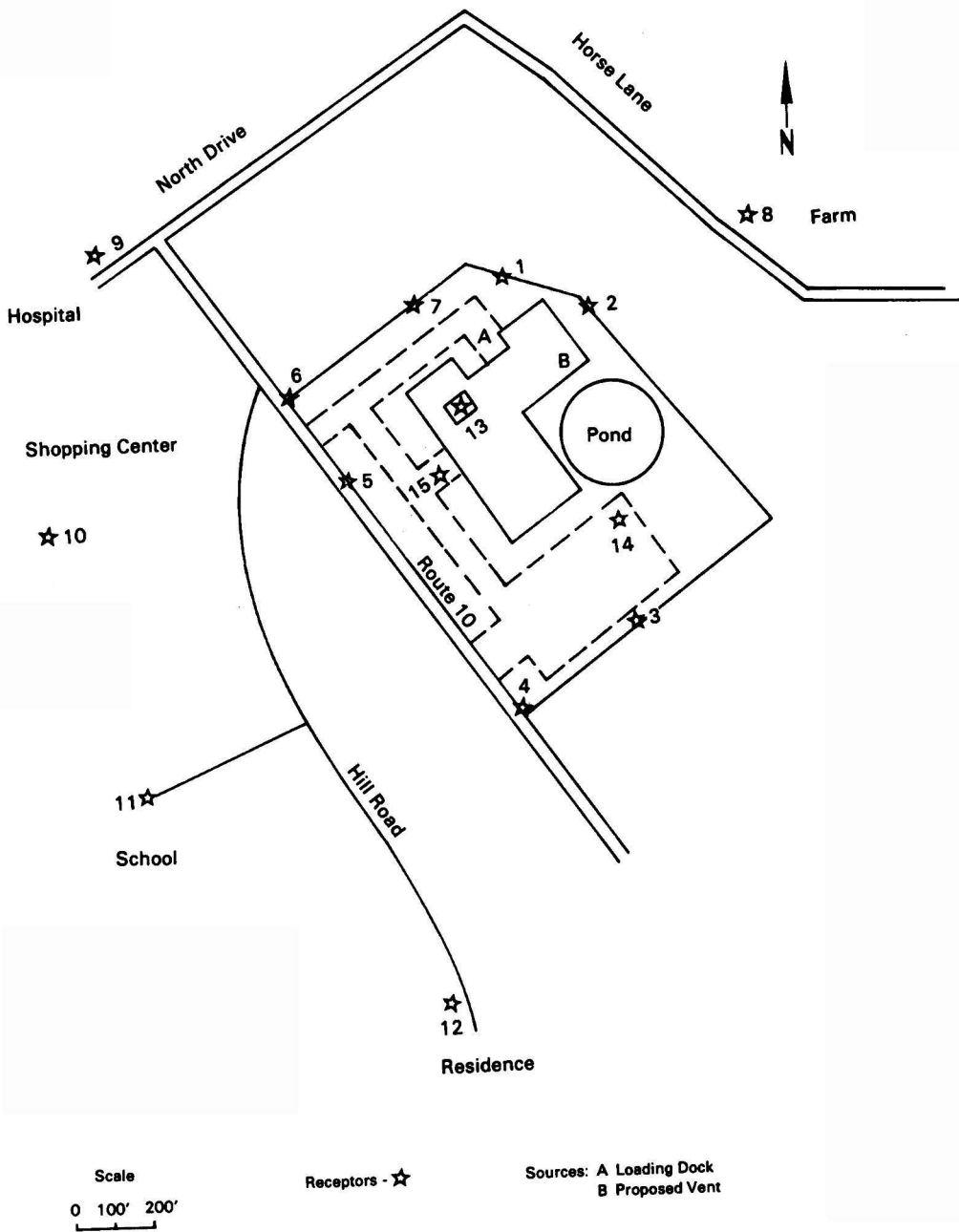


Figure 1. Location of sources and receptors for the case study.

estimate the maximum short-term concentration from an episodic release. For slow leaks that are steady over several minutes, the standard ISC model is appropriate because emissions disperse more in the form of a continuous plume rather than an instantaneous puff.

Results of the worst-case, 1-minute average concentrations for accidental releases are shown in Table 8. For the loading dock both chlorine and ammonia result in peak 1-minute concentrations above the IDLH. In contrast, results for the release, emitted into the vented cabinet and through the rooftop stack indicate that only receptor to ex-

perience concentrations exceeding the IDLH would be the fresh air intake located on the roof.

For this case study the climatological frequency of meteorological conditions have been derived from measurements taken at a local airport as illustrated in Figure 3. This figure indicates that there is a much higher probability that winds would transport an atmospheric release towards the east than towards the west. Table 9 shows how the predicted chlorine concentrations for the loading dock release would vary at each receptor according to this meteorological probability.

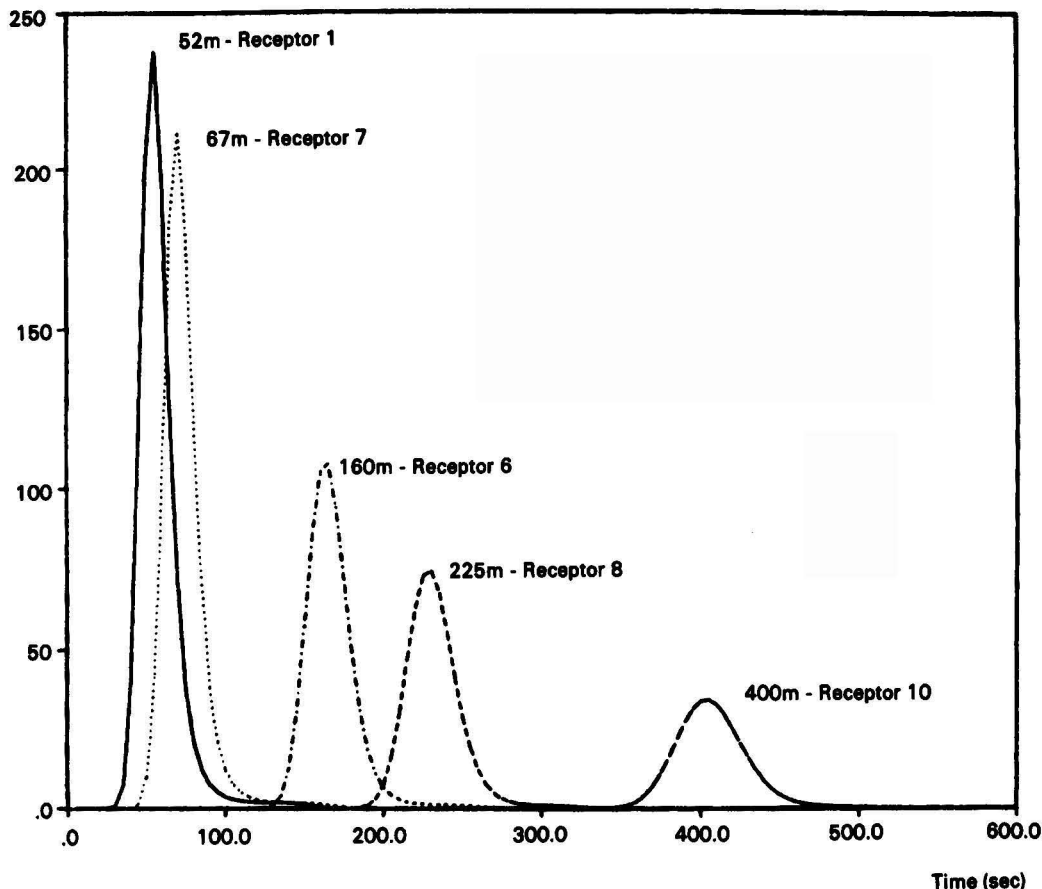


Figure 2. Maximum chlorine concentration for a ground level release as a function of time for various downwind distance.

Evaluating the Health Effects of Acute Exposure

In the dispersion modeling analysis, the peak 1-minute average concentration is used as a conservative benchmark for acute toxic exposures, that is, it represents a longer time than most people could hold their breath in an emergency situation. If the 1-minute concentration is below the IDLH level then one can be reasonably assured that there will be no lasting health effects resulting from an acute exposure [4].

In this present application the IDLH which is defined on the basis of preventing symptoms which would interfere with life-saving evacuation is compared to an acute 1-minute concentration. A lower value, the Short Term Exposure Limit (STEL) is more generally used as the reference value for evacuation planning but is compared to a 15-minute average concentration. The specific guideline and time averaging approach selected by the analyst will depend to some degree on the duration of the release and emergency planning goals defined for a specific case.

Multiple Chemical Exposure

The previous analysis evaluated the degree of health-related impacts as measured against the IDLH for the release of individual chemicals. Although much more remote, the possibility of releasing two or more gases is also of interest.

How the simultaneous exposure to multiple chemicals will affect humans depends upon the site and mechanisms of effect within the body. Effects may be antagonistic, independent, additive, or synergistic. For instance,

TABLE 8. WORST-CASE 1-MINUTE IMPACTS IN TERMS OF PERCENT OF THE IDHL⁺ FOR RELEASES AT THE LOADING DOCK (A) AND THROUGH ROOFTOP VENTS (B)

Receptor	Chlorine		Ammonia		Arsine	
	A	B	A	B	A	B
1	356	36	122	12	75	8
2	340	48	115	16	70	10
3	180	40	59	14	38	8
4	152	40	50	14	32	8
5	240	56	78	19	50	12
6	224	44	73	15	47	9
7	336	40	113	14	70	8
8	176	56	58	19	37	12
9	116	20	38	7	25	4
10	100	40	33	14	22	8
11	88	40	29	14	18	8
12	76	28	25	10	17	6
13	390	220	132	75	82	46
14	210	35	71	12	44	7
15	266	40	90	14	56	8

⁺IDLH: chlorine—25 ppm
ammonia—550 ppm
arsine—6 ppm

Annual (1969 - 1973)

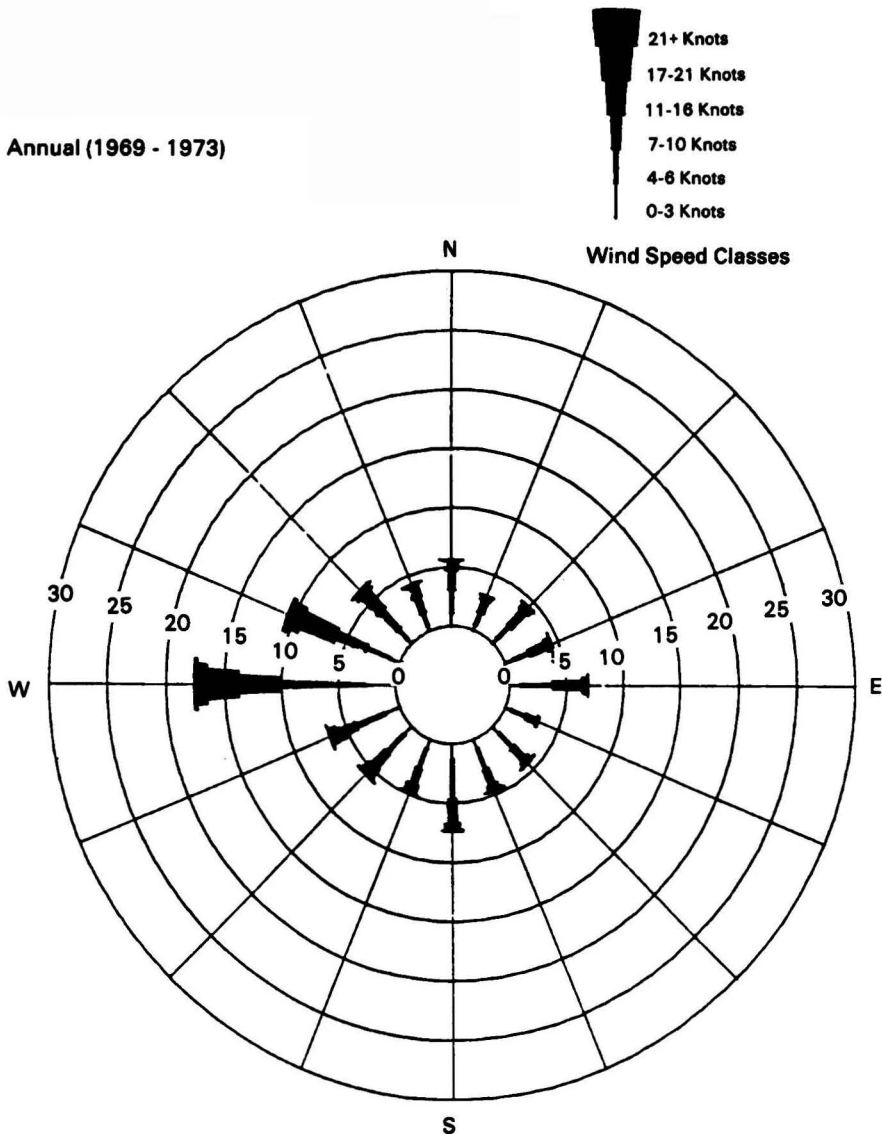


Figure 3. Wind rose for local airport used in the frequency analysis.

if one gas chemical causes a decrease in respiration rate, it may antagonize the impact of the second gas, because a smaller dose of the second gas is being received by the body. In another instance, one gas may affect the central nervous system while the other affects the kidney. The effects in this case may be more nearly independent. Additivity is often encountered when mechanisms of toxicity are similar, as was assumed to be the case for chlorine and ammonia in our case study. Synergism is the interesting phenomenon where the toxic effect of a combined exposure is greater than the sum of the individual effects. For instance, sulfur dioxide combined with non-toxic levels of sub micron zinc oxide aerosols under the appropriate conditions of temperature and humidity becomes more toxic than sulfur dioxide alone (this is due in part to oxidation of sulfur dioxide to the more irritant sulfite and sulfates) [5].

It may be useful to represent these risk assessment methods as a mathematical expression. Consider a health

effect measure, E , which indicates an unacceptable risk if it exceeds unity (one). For exposure to a single gas we have suggested

$$E_1 = \frac{\chi_1}{A_1 \cdot IDLH_1} \quad (1)$$

where χ is a 1-minute concentration and "A" indicates what multiple or fraction of the IDLH represents an acceptable risk. When concentrations of two gases are considered that act with similar mechanisms we can write:

$$E_{12} = I \left[\frac{\chi_1}{A_1 \cdot IDLH_1} + \frac{\chi_2}{A_2 \cdot IDLH_2} \right] \quad (2)$$

Where I is an "interaction" factor for the two compounds, I would be less than one if the compounds were antagonistic, one if the toxic effects were additive, and greater than one for synergistic actions. Application of a

TABLE 9. METEOROLOGICAL PROBABILITY ANALYSIS
 1-MINUTE IMPACT OF CHLORINE (PPM) LOADING DOCK—
 SOURCE A
 IDLH = 25 PPM

Receptor	Highest	Probability*	
		1%	5%
1	89	89	20
2	85	85	34
3	45	19	9
4	38	17	5
5	60	25	—
6	56	23	13
7	84	34	—
8	44	44	19
9	29	14	5
10	25	12	4
11	22	8	—
12	19	10	2
13	98	56	18
14	52	22	10
15	66	33	9

*Probability that in the event of an accidental release that the concentration at each receptor would exceed the values in the table (*i.e.*, at receptor 1 the concentration would exceed 20 ppm 5% of the time)

value for I is combination-specific and requires a great deal of professional judgement.

Both chlorine and ammonia are strong respiratory irritants affecting skin, eyes, and membranes of the nose, throat and lungs. Because their mode of action is so similar, we suggest that the above equation may be suggested

as a method to assess the combined acute health effects (with $I = 1$). In contrast, arsine is not an irritant, but a nerve and blood poison [6]. Simultaneous exposure to arsine plus chlorine or ammonia could therefore be evaluated independently using Equation (1).

SUMMARY

This generalized risk assessment approach is applicable to a wide variety of industrial facilities. The results of such a study can help to manage risks at existing sites and plan for an emergency response program. For facilities that are still in the planning stage, such an assessment can also help to produce a design that optimally reduces both on-site and off-site risks.

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Important Issues Related to Air Pollution at Municipal Solid Waste Facilities

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This paper presents a discussion of municipal solid waste (MSW) combustion and emission control. The issues of combustion technology, of available air pollution control systems, and of public health are explored in order to present an overview of the state-of-the-art of combustion and air pollution control at facilities that burn unprocessed MSW or processed forms such as refuse-derived fuel (RDF). The discussion also includes a presentation of the results of a study sponsored by the Minnesota Pollution Control Agency (MPCA), and performed by Cal Recovery Systems, Inc. (CRS), for the purpose of assisting the MPCA in the development of performance and operating guidelines for MSW combustion facilities to be sited in Minnesota.

INTRODUCTION

While the incineration of MSW has been practiced extensively in Europe and Japan, it is exhibiting a renaissance in the United States as landfill capacity here becomes increasingly scarce. The initial growth of incineration in the 1950s and 1960s in the U.S. was thwarted by increasingly stringent air pollution regulations, the result being the virtual abandonment of the concept at the closeout of the 60s. With the renewed interest in incineration, questions have arisen regarding the impact of incineration technologies on public health and the environment. These important issues are discussed here along with the results of a field evaluation of an incinerator conducted by CRS for the Minnesota Pollution Control Agency (MPCA). The incinerator is located in the City of Red Wing, Minnesota. Recommendations are presented that are based on the results of the study. While the recommendations are intended for the use of the MPCA, many apply as well to the country as a whole.

Two general types of technologies for burning MSW are available: mass burn incineration and processed waste fuel (i.e., RDF) systems. Mass burn facilities combust MSW with little or no processing. Processing MSW involves a series of steps to segregate combustible materials from those that are noncombustible. Collectively, the combustible materials are known as refuse-derived fuel (RDF). The characteristics and combustion properties of unprocessed MSW and of RDF differ, and the differences form a substantial impact on the operating conditions and equipment required for efficient and environmentally sound combustion processes.

Air pollution control is directed towards the control of two forms of stack gas emissions, namely, solid and gaseous effluents. Both criteria and non-criteria pollutants

are generated as a consequence of the combustion of solid waste. The criteria pollutants are: particulate matter, nitrogen oxides, sulfur oxides, carbon monoxide, and lead. The non-criteria pollutants include: heavy metals, and toxic organic compounds.

Based upon the review of the literature, the following combustion and post-combustion methods are available for control of stack gas emissions:

Pollutant	Control Methods	Typical Reduction (%)
NO _x	selective catalytic reduction, selective non-catalytic reduction, flue gas recirculation, combustion control	10 to 60
Acid Gases (SO ₂ and HCl)	wet scrubber, dry scrubber, fabric filter, electrostatic precipitator	50 to 85 SO ₂ , 75 to 90 HCl
CO	combustion control	50 to 90
Heavy Metals	dry scrubber, fabric filter, electrostatic precipitator	70 to 95
Particulates	electrostatic precipitator, fabric filter	95 to 99.9
Toxic Organics (PCDD, PCDF, etc.)	combustion control, combination of dry scrubber and fabric filter	50 to 99.9

In addition to combustion and post-combustion methods of control, pollutant emissions may be reduced in some circumstances through the control of particular characteristics of the solid waste feedstock. For example, the input burden of certain heavy metals may be reduced through source separation or through mechanical processing of MSW into a refuse-derived fuel largely devoid of metallic waste containing heavy metals.

PUBLIC HEALTH RISKS

Published information on the subject of health risk assessments of MSW combustion facilities available through April 1986 was reviewed and summarized. The

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reader should bear in mind that the health risk assessments described in the literature are based in many cases on input data of unknown accuracy and precision, e.g., emission factors of unknown precision and of unknown relation to the project being analyzed in terms of impacts to the public health. Some of the key findings of the literature review are described below.

Available information seems to indicate that the following would limit emissions of criteria pollutants from resource recovery facilities: 1) the oversight and supervision by regulatory authorities; and 2) the accumulated experience and familiarity of control of criteria pollutant emissions. Consequently, if properly controlled, emissions of criteria pollutants from incineration facilities would not cause health problems.

Based on evaluations by representatives of the U.S. EPA, it has been estimated that if the upper range of 2,3,7,8-TCDD concentration in the air is 0.092 $\mu\text{g}/\text{m}^3$, the cancer risk for lifetime inhalation exposure would be between zero to 8-19 chances in one million at the 95 percent level of confidence.

At this time, it may be concluded that in the large majority of cases of TCDD exposure in man, chloracne is most likely to be the first and most commonly observed sign of toxicity. This empirical relationship, however, is not absolute.

From clinical experience, the principal short-term (acute) and long term (chronic) toxic effects of 2,3,7,8-TCDD are chloracne and changes in liver function, respectively. From animal studies, the data indicate that exposure to 2,3,7,8-TCDD may increase the risks of neoplasia, but only in certain organs and the likelihood of effect may depend on gender.

From estimates of the ground level concentrations of TCDD equivalents resulting from resource recovery facilities, it can be stated that the chances of developing short-term (i.e., acute) toxicity from dioxins are virtually non-existent. From clinical experience and animal studies, it is known that acute toxic effects have thresholds. The dosages that are commonly estimated to occur as a result of emissions from resource recovery facilities are approximately one hundred thousand times below the dosages required for acute toxicity.

Small percentages of metals are present in both the organic and inorganic fractions of refuse. When the refuse is combusted, some of these metals are emitted into the air. For most metals, the safety factors exceed 1,000 when projected exposure doses are compared to the TLV/30. Similarly, large margins of safety also exist for most metals when compared to the background levels in urban air or to levels of metals in the diet.

The ground level concentrations of metals predicted for resource recovery facilities are too small to have acute toxic effects. Computer model predictions of 8-hr or 24-hr maximum ground level concentrations in most cases are substantially less than 5 percent. Such contributions from a resource recovery facility to normal daily intake are not likely to produce adverse effects.

The "no observable adverse effect level (NOAEL)" of 2,3,7,8-TCDD in animals of 1 nanogram/kg body weight/day can be utilized as an important point of reference for setting acceptable exposure levels. The fraction of the NOAEL considered to be acceptable for human exposure as well as estimates of the overall bioactive dose vary for different regulatory agencies.

In the future, decisions on acceptable dosages (and concomitantly emissions) of dioxins and on safeguarding the public health will be facilitated if attention and consensus can be focused on the choice of safety factors to be applied to the NOAEL.

RED WING INCINERATOR FIELD TEST PROGRAM

The Red Wing incinerator facility receives residential, commercial, and industrial waste from and around the City of Red Wing. The facility burns about 100 tons per day of solid waste in a modular two-stage incinerator. The incinerator is comprised of two primary combustion chambers, one common secondary combustion chamber, a waste heat boiler, and a two-field electrostatic precipitator.

Municipal Solid Waste Characterization

Field test programs to determine the characteristics of the wastes disposed at the Red Wing Incinerator Facility were carried out in May and September, 1986. Determinations of heavy metal concentrations as well as ultimate, proximate, and heating value analyses of the combustible fraction of Red Wing MSW were performed only during the September 1986 field test program. The concentrations of heavy metals found in the combustible fraction of the waste sampled in September are described in Table 1. In the table, concentrations of metals found in Red Wing are compared to those found in the combustible fraction of MSW at several other locations in the U.S. The ultimate analyses and proximate analyses (including heating value) of the combustible fraction are reported in Tables 2 and 3, respectively. Some comparative data reported for other locations in the U.S. are also shown in the tables.

Characterization of Incinerator Effluent Streams

A summary of the major constituents found in the stack gas from the Red Wing Incinerator is presented in Table 4. The low CO concentration is most likely attributable to air leakage into the flue gas duct downstream of the boiler. The concentrations of metals found in the stack gas, in the bottom ash, and in the precipitator ash are summarized in Table 5. The concentrations of metals found in the combustible fraction of Red Wing MSW during the time of emission testing also are shown in Table 5 for the purpose of reference. The data in the table show that the concentration of a particular metal in the precipitator fly ash is, in most cases, greater than that in the bottom ash. For metals with low boiling points (such as lead, zinc, and mercury), the concentration in the fly ash was found to be several orders of magnitude greater than that in the bottom ash.

Summaries of concentrations of PCDDs and PCDFs found in the stack gas from the Red Wing incinerator are presented in Tables 6 and 7, respectively. The totals of mono- through octa-PCDD and PCDF are 967 and 1113 ng/m^3 , respectively, reported as actual measured values. The average concentrations of PCDD and PCDF measured at the Red Wing incinerator are compared with those of other waste combustion facilities in Table 8.

Summaries of the concentrations of PCDDs and PCDFs found in the bottom ash and precipitator ash residues of the Red Wing incinerator are shown in Tables 9 and 10, respectively. In nearly all cases, the concentration of specific PCDD and PCDF species in the precipitator fly ash were found to be several orders of magnitude greater than those in the bottom ash. The results are comparable to those found at other incinerator sites.

The stack gas emissions of the Red Wing incinerator test program are compared to those of the Prince Edward

TABLE 1. COMPARISON OF RANGE OF CONCENTRATION OF HEAVY METALS ($\mu\text{g/g}$) IN COMBUSTIBLE FRACTION OF MSW ENTERING RED WING INCINERATOR WITH OTHER SITES

Metals Analysis	Red Wing ^{a)} MN	No. Calif. County CA	North Santa Clara County CA	San Diego CA	Ames IA	Seattle WA
Arsenic	0.4-3.3	11-654	7	10		1-2.4
Selenium	3.3-8	<4	<0.4	0.5	8	0-0.1
Mercury	0-13	<0.3	2	0.4		0.5-1
Barium	15-31	27-133	110			37-77
Chromium	30-1512	15-19	21		34	19-34
Lead	85-350	203-797	49	354	613	175-405
Silver	6-17	<0.2	<4			0.5-0.6
Cadmium	0-3.8	<28-35	<3	10	6	2-6
Copper	96-462	110-203	450		572	37-898
Nickel	35-137	525-4870	<15		14	13-21
Zinc	80-2268	126-377	310	871	763	99-275
Antimony	0-4.8	<24-100	<70	3	25	0.9-6
Tin	250-713	53-70	<20	4	27	11-20

a) September 1986 sampling period

TABLE 2. RANGE OF ULTIMATE ANALYSES (PERCENT) OF COMBUSTIBLE FRACTION OF RED WING MSW (MOISTURE-FREE AND ASH-FREE BASIS)^{a)}

Element	Red Wing MN	North Santa Clara County CA	San Diego CA	Ames IA	Baltimore County MD	Chicago IL	Milwaukee WI	St. Louis MO
Carbon	44-53	48.2	50.2	51.5	50.7	54.6	57.0	50.3
Hydrogen	6.6-6.9	6.5	6.7	7.3	7.2	7.2	7.7	7.4
Oxygen	73-49	43.4	40.8	40.0	40.6	36.6	32.7	41.0
Nitrogen	0-1.6	0.3	1.2	0.4	0.8	1.1	1.2	1.0
Sulfur	0.2-0.5	0.23	0.22	0.4	0.7	0.5	0.6	0.4
Chlorine	0.2-0.9	1.2	0.9	0.4	—	—	0.8	—
Fluorine	—	0.0066	—	—	—	—	—	—

a) Totals for columns may not sum to 100 due to round-off error.

TABLE 3. RANGE OF PROXIMATE ANALYSES OF THE COMBUSTIBLE FRACTION OF MSW (OVEN-DRY BASIS)

Parameters	Red Wing MN	North Santa Clara County CA	Ames IA RDF	Baltimore County MD RDF	Chicago IL RDF	Milwaukee WI RDF	St. Louis MO RDF
Ash content (percent)	5-11	10.3	11.8	8.5	27.7	28.2	29.6
Volatile matter (percent)	42-48	78.6	68.7	77.6	62.1	59.8	59.4
Fixed carbon (percent)	12-17	11.1	19.5	13.9	10.2	12.0	11.0
Heating value (Btu/lb)	6230-9230	NA	7500	8600	7000	7200	6200

**TABLE 4. AVERAGE RESULTS OF MAJOR STACK GAS CONSTITUENTS^{a)}
RED WING INCINERATOR STUDY**

Species	Range		3 Run Average ^{b)}
	High	Low	
Particulate matter (gr/ACF) ^{c)}	0.040	0.018	0.030
SO ₂ (ppmv)	169	48	78
O ₂ (percent)	13.7	9.7	12.3
NO _x (ppmv)	196	0	161
CO (ppmv) ^{d)}	13	0	1
CO ₂ (percent)	9.5	5.2	7.6
HCl (ppmv) ^{c)}	624	339	473

a) Actual values on a dry weight basis except as noted.

b) Average of average values for each run.

c) Wet weight basis.

d) See text for discussion of circumstances related to the abnormally low CO readings.

Island (PEI) incinerator in Table 11. Both incinerators are of similar design. Thus, the comparison is of interest. When interpreting the data in Table 11, the reader should bear in mind that the results have not been corrected for the composition of the feedstock MSW. In comparing the data, it is interesting to note that the PCDD and PCDF emissions for the Red Wing incinerator are about an order of magnitude greater when measured on a volumetric basis than those measured at the PEI incinerator. The PCDD and PCDF emissions are greater despite the low CO levels (less than 2 ppm) measured at Red Wing. As mentioned earlier, air leakage downstream of the boiler most likely caused the low CO concentration and may have in fact fostered conditions conducive to the formation of PCDDs and PCDFs.

Complete combustion (as indicated by low CO levels) is considered by some to be necessary for maximizing the destruction and minimizing the formation of PCDD's and

TABLE 5. SUMMARY OF METAL CONCENTRATIONS IN VARIOUS INPUT AND OUTPUT STREAMS
RED WING INCINERATOR STUDY

Element	Waste Stream Combustible Fraction Only µg/g	Stack Gas		Ash Residues	
		Vapor Phase µg/Nm ³ Standard ^{a,b}	Solid Phase µg/Nm ³ Standard ^{a,b}	Bottom Ash µg/g	Precipi- tator Ash µg/g
Silver	12.6	3.27	5.71	0.90	9.0
Aluminum	NM ^c	72.7	40.1	30,000	39,000
Arsenic	2.1	109	14.6	30	300
Boron	NM	291	29.3	60	60
Barium	18.1	3.27	12.5	92	490
Beryllium	NM	0.363	0.049	0.10	1.0
Calcium	NM	33.1	367	26,000	42,000
Cadmium	0.9	1.09	206	5.7	2,000
Cobalt	NM	3.63	0.488	1.0	10
Chromium	263.9	3.27	24.9	300	1,100
Copper	312.9	3.63	117	110	910
Iron	NM	56.6	245	35,000	14,000
Potassium	NM	109	5,560	5,100	34,000
Magnesium	NM	36.3	13.3	3,600	9,900
Manganese	NM	1.09	15.1	300	490
Molybdenum	NM	18.2	2.44	5.0	50
Sodium	NM	196	6,840	12,000	48,000
Nickel	100.5	7.27	0.977	19	20
Lead	255.0	18.2	3,440	170	15,000
Antimony	NM	21.8	93.0	6.0	480
Selenium	6.2	109	14.6	30	300
Silicon	NM	109	14.6	59,000	67,000
Thallium	NM	32.7	4.38	9.0	90
Vanadium	NM	7.27	0.977	10	10
Zinc	503.1	2.18	16,200	1,500	110,000
Mercury	8	8.6 ^d	605 ^e	0.025	4.4

a) Corrected to 7 percent O₂, 1 atm, 68 F, dry weight basis.

b) Values below the detection limits of the analytical equipment are in some cases included in the average. For analyses where one (or all of the actual) test value(s) was below the detection limit of the instrumentation, the actual value was estimated as 0.5 times the detection limit.

c) NM = species was not measured.

d) Present as elemental mercury.

e) Mercury present in the form of mercury salts.

TABLE 6. SUMMARY OF POLYCHLORINATED DIBENZODIOXIN CONCENTRATIONS IN STACK GAS^a
RED WING INCINERATOR STUDY

	3 Run Average	
	ng/m ³ Actual	ng/Nm ³ Standard ^b
Total monochlorodibenzodioxin	0.00268	0.004473
Total dichlorodibenzodioxin	0.002511	0.004185
Total trichlorodibenzodioxin	3.67	6.07
2,3,7,8-tetrachlorodibenzodioxin	0.165481	0.279328
Total tetrachlorodibenzodioxin	45.40	44.40
1,2,3,7,8-pentachlorodibenzodioxin	7.82	12.95
Total pentachlorodibenzodioxin	167.30	276.67
1,2,3,4,7,8-hexachlorodibenzodioxin	10.56	17.55
1,2,3,6,7,8-hexachlorodibenzodioxin	29.53	48.93
1,2,3,7,8,9-hexachlorodibenzodioxin	42.27	70.00
Total hexachlorodibenzodioxin	291.33	482.67
1,2,3,4,6,7,8-heptachlorodibenzodioxin	138.20	228.67
Total heptachlorodibenzodioxin	274.00	454.00
Octachlorodibenzodioxin	185.23	306.67
Total mono-octa chlorodibenzodioxin	967	1570

a) Values below the detection limits of the analytical equipment are in some cases included in the average. For analyses where one (or all of the actual) test value(s) was below the detection limit of the instrumentation, the actual value was estimated at 0.5 times the detection limit.

b) Standard: corrected to 7 percent O₂, 1 atm, 68°F, dry weight basis.

TABLE 7. SUMMARY OF POLYCHLORINATED DIBENZOFURAN CONCENTRATIONS IN STACK GAS^{a)}
RED WING INCINERATOR STUDY

	3 Run Average	
	ng/m ³ Actual	ng/Nm ³ Standard ^{b)}
Total monochlorodibenzofuran	0.002511	0.004185
Total dichlorodibenzofuran	0.205436	0.339631
Total trichlorodibenzofuran	28.8	47.5
2,3,7,8-tetrachlorodibenzofuran	35.9	59.4
Total tetrachlorodibenzofuran	211.4	350
1,2,3,7,8-pentachlorodibenzofuran	10.9	18.1
2,3,4,7,8-pentachlorodibenzofuran	46.2	76.4
Total pentachlorodibenzofuran	274.0	453.7
1,2,3,4,7,8-hexachlorodibenzofuran	79.0	130.9
1,2,3,6,7,8-hexachlorodibenzofuran	32.6	54.0
2,3,4,6,7,8-hexachlorodibenzofuran	68.0	112.7
1,2,3,7,8,9-hexachlorodibenzofuran	0.003746	0.006233
Total hexachlorodibenzofuran	293.0	484.7
1,2,3,4,6,7,8-heptachlorodibenzofuran	171.2	283.3
1,2,3,4,7,8,9-heptachlorodibenzofuran	12.7	20.9
Total heptachlorodibenzofuran	258.7	428.0
Octachlorodibenzofuran	46.8	77.5
Total mono-octa chlorodibenzofuran	1113	1842

a) Values below the detection limits of the analytical equipment are in some cases included in the average. For analyses where one (or all of the actual) test value(s) was below the detection limit of the instrumentation, the actual value was estimated at 0.5 times the detection limit.

b) Standard: corrected to 7 percent O₂, 1 atm, 68°F, dry weight basis.

PCDFs. The results of the Red Wing incinerator test program indicate that despite the presence of low concentrations of CD in the stack gas, the manner of reaching the low CO concentrations (i.e., incinerator operating condi-

tions) is important in achieving low emissions of PCDDs and PCDFs. When interpreting the PCDD and PCDF emissions for the Red Wing incinerator in comparison to other facilities, the reader should bear in mind also that

TABLE 8. TEST DATA FOR PCDD AND PCDF AND CARBON MONOXIDE

Facility	Size	Fuel ^{o)}	Control Equipment ^{a)}	CO (ppm) ^{b)}	PCDD + PCDF (ng/dscm)	TEF (ng/dscm) ^{c)}
Quebec City, Canada	205 ^{d)}	MSW	SD/BH	(200)	1	0
Linköping, Sweden	400	MSW	SD/BH	(100)	—	<0.1
Marion Co., Oregon	550	MSW	SD/BH	16	1.6	0.1
Wurzburg, West Germany	660	MSW	SD/ESP	35	50	0.4
Pittsfield, Mass.	100	MOD	ESP	23	24.3	NA
Oneida Co., New York	200	MOD	ESP	NA	187	1.1
Pr. Ed. Island, Canada	100	MOD	None	40	143	1.4
Cattaraugus, New York	120	MOD	None	NA	257	2.8
Tulsa, Oklahoma	750	MSW	ESP	(32)	53	0.7
Peekskill, New York	2,250	MSW	ESP	22	74	1.4
Stuttgart, West Germany		MSW	ESP	NA	476	3.0
Umea, Sweden	140	MSW	ESP	NA	413	3.6
Chicago NW, Ill.	330	MSW	ESP	70	280 ^{e)}	5.2
Albany, New York	250	RDF	ESP	195	223	5.6
Andover, Mass.	1,500	MSW	ESP	33	460	6
Niagara Co., New York	2,400	RDF	ESP	NA	1,546	19.5
Avesta 2, Sweden	120	MSW	ESP	(200)	1,716	21
Avesta 1, Sweden	120	MSW	ESP	(3,400)	3,922	47
Philadelphia, Penn.	750	MSW	ESP	205	3,600	59
Hampton, Virginia	100	MSW	ESP	(2,300)	9,844	106
Hamilton, Canada	250	RDF	ESP	700	8,820	112
Red Wing, Minnesota	100	MOD	ESP	2 ^{d)}	3,412	27

a) SD/BH: spray dryer/baghouse; ESP: electrostatic precipitator

b) Values in parentheses are maximum values for the test period. All other values shown are averages for the test period.

c) TEF are 2,3,7,8, toxic equivalents by the EPA method.

d) The tests at Quebec City were performed on a small part of the flue gas in a pilot-scale dry scrubber.

e) Penta dioxins and furans were not measured. Approximate values were used.

f) MSW: large raw municipal waste incinerator; MOD: modular municipal waste incinerator; RDF: refuse-derived fuel

g) The value is low due to air leakage into the flue gas system.

TABLE 9. POLYCHLORINATED DIBENZODIOXIN CONCENTRATIONS IN ASH RESIDUES (ng/g)^{a)}
RED WING INCINERATOR STUDY

	Bottom Ash Average	Precipitator Ash Average
Total monochlorodibenzodioxin	0.000666	0.005
Total dichlorodibenzodioxin	0.000833	0.48
Total trichlorodibenzodioxin	0.001166	9.50
2,3,7,8-tetrachlorodibenzodioxin	0.001	0.53
Total tetrachlorodibenzodioxin	0.001	38.33
1,2,3,7,8-pentachlorodibenzodioxin	0.001	5.90
Total pentachlorodibenzodioxin	0.004	107.00
1,2,3,4,7,8-hexachlorodibenzodioxin	0.001666	8.97
1,2,3,6,7,8-hexachlorodibenzodioxin	0.001666	18.00
1,2,3,7,8,9-hexachlorodibenzodioxin	0.002	33.00
Total hexachlorodibenzodioxin	0.057333	213.33
1,2,3,4,6,7,8-heptachlorodibenzodioxin	0.07	116.33
Total heptachlorodibenzodioxin	0.15	220.00
Octachlorodibenzodioxin	0.138666	159.00

a) Values below the detection limits of the analytical equipment are in some cases included in the average. For analyses where one (or all of the actual) test value(s) was below the detection limit of the instrumentation, the actual value was estimated as 0.5 times the detection limit.

TABLE 10. POLYCHLORINATED DIBENZOFURAN CONCENTRATIONS IN ASH RESIDUES (ng/g)^{a)}
RED WING INCINERATOR STUDY

	Bottom Ash Average	Precipitator Ash Average
Total monochlorodibenzofuran	0.0007	0.050
Total dichlorodibenzofuran	0.0005	1.240
Total trichlorodibenzofuran	0.0008	28.667
2,3,7,8-tetrachlorodibenzofuran	0.0038	17.333
Total tetrachlorodibenzofuran	0.0038	72.667
1,2,3,7,8-pentachlorodibenzofuran	0.0005	3.533
2,3,4,7,8-pentachlorodibenzofuran	0.0007	13.000
Total pentachlorodibenzofuran	0.0005	83.667
1,2,3,4,7,8-hexachlorodibenzofuran	0.0040	31.000
1,2,3,6,7,8-hexachlorodibenzofuran	0.0010	10.433
2,3,4,6,7,8-hexachlorodibenzofuran	0.0012	20.667
1,2,3,7,8,9-hexachlorodibenzofuran	0.0012	0.0012
Total hexachlorodibenzofuran	0.0203	105.667
1,2,3,4,6,7,8-heptachlorodibenzofuran	0.0152	74.333
1,2,3,4,7,8,9-heptachlorodibenzofuran	0.0033	3.867
Total heptachlorodibenzofuran	0.0213	112.667
Octachlorodibenzofuran	0.0098	21.000

a) Values below the detection limits of the analytical equipment are in some cases included in the average. For analyses where one (or all of the actual) test value(s) was below the detection limit of the instrumentation, the actual value was estimated as 0.5 times the detection limit.

TABLE 11. COMPARISON OF STACK EMISSION DATA FROM TWO MODULAR INCINERATORS—
PRINCE EDWARD ISLAND (PEI) AND RED WING^{a)}

	Stack Gas Temp. (°F)	CO ₂ (%)	O ₂ (%)	Parti- culate ^{b)} mg/Nm ³	CO ^{b)} ppm	SO ₂ ^{b)} ppm	NO _x ^{b)} ppm	PCDD ^{b)} ng/Nm ³	PCDF ^{b)} ng/Nm ³	Total PCDD PCDF ^{b)} ng/Nm ³	HCl ^{b)} mg/Nm ³
Prince Edward Island											
Normal	363	8	12	217	70	64	322	111	149	260	1,131
Long cycle	363	8	12	240	42	86	282	111	163	274	1,115
High secondary temperature	361	10	10	262	35	80	274	66	101	167	1,238
Low secondary temperature	266	7	13	171	53	89	300	126	101	227	975
Red Wing											
Average	520	8	12	113	1.6 ^{c)}	126	260	1,570	1,842	3,412	1,235

a) An electrostatic precipitator provided air pollution control at each site.

b) Dry, corrected to 7 percent O₂.

c) The value is low due to air leakage into the flue gas stream.

TABLE 12. STACK EMISSION FACTORS (MASS PER MG OF MSW INPUT)

Prince Edward Island

	Red Wing Average	Normal Condition	Long Cycle	High Secondary Temperature	Low Secondary Temperature
TSP (g/Mg)	736	843	874	977	682
HCl (g/Mg)	8,529	4,400	4,130	4,480	3,930
PCDD (µg/Mg)	10,450	428	400	228	516
PCDF (µg/Mg)	12,023	570	574	340	411
Cadmium (g/Mg)	1.3	3.8	3.0	3.2	2.6
Lead (g/Mg)	22.6	54.8	57.8	60.0	34.2
Chromium (g/Mg)	0.1	0.2	0.1	0.4	0.1
Nickel (g/Mg)	0.05	1.0	1.0	2.2	1.9
Mercury (g/Mg)	3.9	2.8	2.0	3.6	2.2
Antimony (g/Mg)	0.7	2.3	9.6	2.1	1.9

the flue gas temperature is 100° to 200°F above that typical of the operation of the other modular waste combustion facilities.

Based upon the throughput of MSW, stack emission factors have been calculated for the Red Wing incinerator and are compared with those of the PEI incinerator in Table 12. The emission factors for most pollutants are similar. Notable exceptions are higher factors determined for the Red Wing incinerator facility for HCl, PCDD, and PCDF and lower factors for lead and nickel.

CONCLUSIONS

Combustion of MSW with energy recovery is a technology that recently has received a considerable amount of attention in the U.S. In particular, the state of Minnesota has experienced a substantial interest in MSW combustion as an alternative to landfill disposal of solid waste.

A certain amount of data is available on the type and amount of pollutants emitted from waste combustion facilities. A substantial amount of the information was collected before 1980, in several cities in the U.S. and other countries under various conditions (i.e., not corrected to 12 percent CO₂). Test data on air pollutants generally are converted to "emission factors" (lb/ton or lb/MBtu) using assumed throughput, heating value for the waste, or both. An error on the order of 10 percent in estimating the flow rate through the plant combined with a similar error in estimating or calculating the heating value of the waste would result in an error of about 20 percent when the emission factor is reported in lb/MBtu.

A few studies have been carried out to compile available emission factors from waste combustion facilities. These studies generally compile data with little rigorous scrutiny or interpretation of the quality of the data or the conditions under which the information was obtained. Virtually no statements of accuracy nor precision of the data are presented in studies concerning waste combustion. Recent and planned studies in Sweden and North America will be reporting data more completely. Collection of these data will significantly aid in the analysis of health risks and in the establishment of proper operating conditions for incinerators.

Toxicologists and other specialists use emission factors from waste-to-energy facilities, mathematical models for dispersion (to predict concentrations of pollutants at ground level), and dose-response relationships to estimate public health effects of emissions generated by waste combustion sources. Oftentimes, emission factors from one location are used for another location with inadequate consideration of the consequences, for example, of potential changes in the factors due to differences in the composition of the waste, the presence or absence of

certain air pollution control equipment, or operating conditions.

Based upon the review of health risk assessment studies for waste combustion facilities, emission of pollutants will not cause long-term public health effects provided that the following conditions are met:

- a. Levels of emissions from waste processing facilities are of the same order of magnitude as those reported in the present study (i.e., emissions are not higher due to poor control, change in waste properties, or operating conditions).
- b. Background pollutant levels are not greater than air quality standards for criteria pollutants.
- c. Body loading of pollutants is substantially less than levels that cause unacceptable risks.

Over the past five years, the health risks associated with waste combustion facilities have been a subject of intense scrutiny, debate, and research. The present rate of generation of information and data on non-criteria pollutants is substantial and the risks associated with them may change as more and better information is collected and made available.

It has only been within the last few years that communities have started to carry out waste characterization analyses. Reliable information on the composition and characteristics of solid waste and how they change as a function of time are found to be lacking and insufficient in many cases to make sound engineering design decisions regarding the generation and control of pollutants.

The particulate emissions measured in the stack gas of the Red Wing incinerator were of the same order of magnitude as those reported for a unit equipped with a baghouse. Electrostatic precipitator (ESP) operation was less than optimal during testing at Red Wing. At the time of the emission testing, only one field of the ESP was in operation. Particulate emissions will likely be less than the reported values when both ESP fields are in operation.

Concentrations of criteria pollutants measured in the stack gas of the Red Wing facility showed that most emissions were similar to those obtained at other facilities.

Emission factors for PCDD and PCDF calculated for the Red Wing facility were approximately twenty to forty times greater than those calculated for a similar facility in Canada (i.e., Prince Edward Island). The calculated emission factor for HCl was approximately twice that calculated for the Prince Edward Island incinerator.

Substantial air leakage into the hot gas stream most likely occurred downstream of the primary combustion chamber during the Red Wing incinerator test program. The routes of air leakage were at the connecting gasket of the secondary combustion chamber and immediately up-

stream of the induction fan. The relatively high concentrations of PCDDs and PCDFs that were measured most likely are attributable wholly or in part to the uncontrolled manner of air introduction through the aforementioned pathways of leakage. Proper maintenance and operation of incinerators should be practiced scrupulously to minimize emissions of organic pollutants, as well as others.

The incinerator field test program identified the importance of sound operating practice for control of the combustion process and of the resultant emissions. Poor operating procedures can and do result in levels of criteria and non-criteria pollutants that are substantially greater than those generated by a well run system.

RECOMMENDATIONS

The following recommendations were formulated based on the results of the study.

Continue to develop a sound and reliable database for the composition of MSW for the state of Minnesota; conduct waste characterization studies on a seasonal basis in various locations around the state; and expand the studies to include the characterization of waste components.

Conduct detailed input/output analyses of waste combustion systems to define and understand the relationship among input waste properties and the characteristics of ash residues, liquid effluents, and stack gas emissions. In particular, mass balances for sulfur, chlorine, heavy metals, and toxic organic compounds are poorly reported in the literature and require considerable research and work effort. Monitor precisely all important operating variables (e.g., throughput, temperature, etc.) throughout the combustion system during the characterization of the solid waste combustion system.

Proceed immediately to define the criteria, parameters, and properties that are important to grant construction and operating permits for refuse combustion systems in terms of each of their effluent streams. Define the units in which data are to be reported in order to standardize data collection methods, reporting, and interpretation. Promulgate the requirements for data collection and reporting on a state-wide basis. In those cases where no, or in-

adequate, methods of measurement exist, structure a program to develop them. Develop a uniform and consistent database for large mass burn systems (>500 TPD); small, modular mass burn systems (<500 TPD); dedicated RDF systems; and dedicated dRDF combustion systems.

Exercise a high degree of caution in utilizing reported emission data (particularly data reported prior to 1980) due to the following reasons:

- a. In an attempt to simplify and standardize the results of air pollution tests, emission factors are determined (i.e., lb/ton or lb/MBtu). Unfortunately, these factors often are calculated using estimates of heating value or of mass throughput. The accuracy, precision, and validity of the emission factors are thus subject to unknown certainty.
- b. Techniques of sample collection and analyses for certain pollutants have, in some cases, changed substantially during the past few years, thus having a serious impact on the validity of comparing and combining data obtained during different time periods. Changes in the techniques of sample collection and measurement have been accompanied by major improvements in accuracy and precision that must be fully understood when interpreting air emission data.
- c. Changes in the composition of MSW within the last 10 years (e.g., plastic, and aluminum) are sufficiently high to have an appreciable effect on the concentration of some pollutants in the stack gases and in the ash residues.

Due to the small database available for incinerators, and the site-specific nature of the waste stream characteristics and of the operating conditions of the facilities, incinerators should be thoroughly tested for the purpose of acquiring data for the conduct of health risk analyses for non-criteria pollutants.

Training programs are needed to educate operators in proper maintenance and control of incinerators, particularly the relationship between performance and operating conditions for the combustion process, the heat recovery system, and the air pollution control system.

The Evaporation Times of Drop Distributions and Their Impact on Costs of In-Duct Humidification Systems for Retrofitting Electrostatic Precipitators

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Retrofit flue gas desulfurization (FGD) systems for utility or industrial boilers installed upstream of an existing electrostatic precipitator (ESP) increase the solids loading and often the resistivity of the solids. These factors can increase the outlet emissions from the ESP. A humidification system installed upstream of the ESP is a cost effective means to restore the performance. The feasibility of installing a humidification system within the existing duct requires having an unobstructed straight section with adequate residence time so that the water drops can completely evaporate. Failure to achieve complete evaporation can lead to the formation of cementitious solids. A method is provided to estimate the evaporation time of typical drop size distributions over the range of humidification and cooling requirements expected for plants with retrofit FGD systems. The evaporation time is strongly dependent on the maximum size drop in the distribution and the approach to the adiabatic saturation temperature that the gas must be cooled to restore the performance of the ESP.

INTRODUCTION

Most of the retrofit FGD systems being developed for utility and large industrial boilers incorporate injection of a calcium or sodium alkali in the boiler or at some location upstream of the ESP. The stoichiometric ratio of alkali added to the inlet SO_2 is typically 2 to 3. The excess reagent and reacted products substantially increase the solids loading to the existing precipitator. Calcium alkali, the most common reagent, can increase the resistivity of the particulate several orders of magnitude. The combination of increased solids loading and increased resistivity can greatly increase the particulate grain loading of the flue gas leaving the ESP. Humidification and cooling of the flue gas upstream of the ESP is one method for restoring of the ESP exit particulate loadings to that which existed before the retrofit system was installed.

Humidification and cooling reduces the volume of gas to be treated, increases the gas density and reduces the resistivity of the particles. The combination of these benefits can often restore the performance of the ESP. The extent of humidification is represented by the approach to the adiabatic saturation temperature of the humidified gas. The approach to adiabatic saturation required to restore ESP performance is dependent on the specific application.

PREVIOUS WORK

A semi-theoretical model of the impact of a calcium based retrofit FGD system on the performance of a precipitator by Helfritsch, *et al.* [1] has shown that it may be

necessary to increase the size by 200 to 600% in order to restore performance. The model also predicts the restoration of ESP performance by alternate methods such as indirect cooling, pulse energization, SO_3 conditioning, and humidification. The validity of the model in predicting the restoration of the performance of an ESP by humidification of the flue gas was confirmed by a pilot plant test program [2] conducted on a 6797 m^3/hr (4000 acfm) slipstream from an industrial boiler. In that pilot plant, calcium reagent was added upstream of a humidification section in the duct.

The size of the humidification section can be estimated from knowledge of the evaporation time of the water drops. Dickinson and Marshall [3] presented a method to compute the evaporation of water drops composed of various size distributions into a gas. More recently Jozewicz and Rochelle [4] presented computations of the evaporation time of slurry dispersions in a spray dryer. Results of their computations were expressed in terms of dimensionless groups and showed that the evaporation time increases as the variance of the distribution increases.

DESIGN OF A HUMIDIFICATION SECTION

Utility boilers typically produce a flue gas of 149°C with an adiabatic saturation temperature of 51°C. With a calcium based retrofit FGD system, the flue gas would have to be cooled to between 65 and 93°C, depending on the application. An in-duct humidification system, shown in Figure 1, consists of a region of the flue duct where

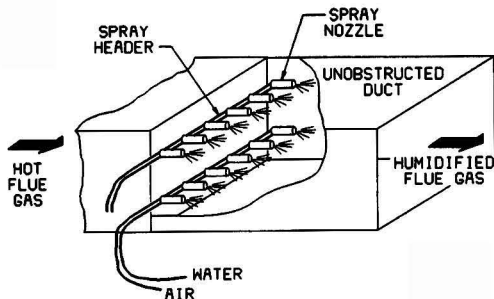


Figure 1. Evaporation section.

nozzles spray water drops cocurrent with the flue gas. Two-fluid nozzles using air as the atomizing fluid are the most common nozzles used to date. The humidification section can be located where the flue gas is flowing horizontally, vertically up, vertically down, or even in an expanding section.

The humidification must be achieved without any wetting of internal walls or other obstructions (*i.e.* turning vanes, internal beams, etc.). Any site where wetting occurs can be expected to lead to the rapid deposition of cementitious solids. Wetted sites will form if the evaporation time required for all the water drops sprayed into the duct exceeds the residence time of the drops in the duct before encountering some surface. If no location within the existing duct is suitable for the humidification then a separate chamber must be installed. This chamber would most likely have a cross section area greater than the existing duct in order to provide the residence time required for the evaporation.

3-Dimensional Fluid Dynamics Model Study

A straight humidification section with an overall residence time greater than that needed for complete evaporation does not insure that wetting will not occur. Wetting could occur if the flue gas has strong eddy currents directed toward the walls of the duct. A 3-dimensional fluid dynamics model study of the humidification section and the components located upstream and downstream are needed to determine if the flow profile is satisfactory and if not, how it might be corrected. Furthermore, the high pressure atomization air used by a two-fluid nozzle could disrupt an otherwise satisfactory flow profile.

SIZING THE HUMIDIFICATION SECTION

The size of the humidification chamber required depends on the evaporation time of the drops. Table 1 shows a discreet drop size distribution for a typical two-fluid nozzle used in humidification systems. A method is needed to predict the evaporation time for drop distributions.

Evaporation Times of Drop Distributions

The mathematical model used to predict the evaporation times for drop distributions in flue gases was originally developed to support the design and operation of the humidifier installed on the pilot plant mentioned earlier [2]. The only restriction on the drop size distribution is that the settling velocity of the maximum size drop in an upflow case must be less than the velocity of the flue gas. The model assumes that the amount of atomization air is small compared to the amount of flue gas so that no cooling of the flue gas occurs by bulk mixing with the

atomization air. If the amount of atomization air is not negligible, then the quantity and temperature of the inlet flue gas used by the model need only be adjusted by assuming it is completely mixed with the atomization air at the entrance to the humidification section. Details of the model are outlined in the Appendix.

Predicted Evaporation Times

The time required for all the drops to evaporate is largely dependent on the size of the largest drops, the approach to the adiabatic saturation temperature that the flue gas must be cooled, and the initial drop size distribution. The influence of the distribution on the evaporation time results from the fact that the smaller drops rapidly consume the bulk of the heat transfer driving force (*i.e.* the temperature difference between the flue gas and drops). During the early evaporation period the largest drops hardly change in size and must evaporate into a flue gas that has had the temperature driving force greatly reduced by the evaporation of the smaller drops.

All of the computations are for the conditions given in Table 2 which are typical for most utility boilers. The initial drop velocity was set 61 m/sec. Calculations with the model have shown that the initial velocity of the drops leaving the nozzle in the direction of the flue gas can vary from 30.5 to 122 m/sec without having any significant effect on the evaporation time.

The maximum size drop which would provide acceptable designs for a humidification system is about 120 microns. As a practical matter nozzles which could produce maximum drops less than 80 microns have extremely low water capacity or require excessive atomization air. Figures 2, 3, and 4 show the results of the computations under the assumption that the distribution consists of only two sizes of drops; those equal to the maximum diameter and those equal to 40% of the maximum diameter. (For two-fluid nozzles, the Sauter mean drop diameter is approximately 40% of the drop diameter of the largest drop.)

Jozewicz and Rochelle [4] reported that increasing the variance of the distribution increases the evaporation time. With a distribution of only 2 sizes, reducing the size of the smaller drop effectively increases the variance. Table 3 shows that an increase in evaporation time occurs when the smaller size drop is decreased. The increase is

TABLE 1. DISCREET DROP SIZE DISTRIBUTION

Drop Diameter (Microns)	Weight percent
8	14
17	19
26	21
36	17
43	12
54	8
66	5
75	2
88	1.5
100	.5

TABLE 2. OPERATING CONDITIONS

Inlet flue gas velocity	10 m/sec.
Inlet flue gas temperature	149°C
Inlet flue gas pressure	1000 kPa
Inlet flue humidity	8.6 mole%
Inlet water temperature	15.5°C
Initial axial drop velocity	61 m/sec.

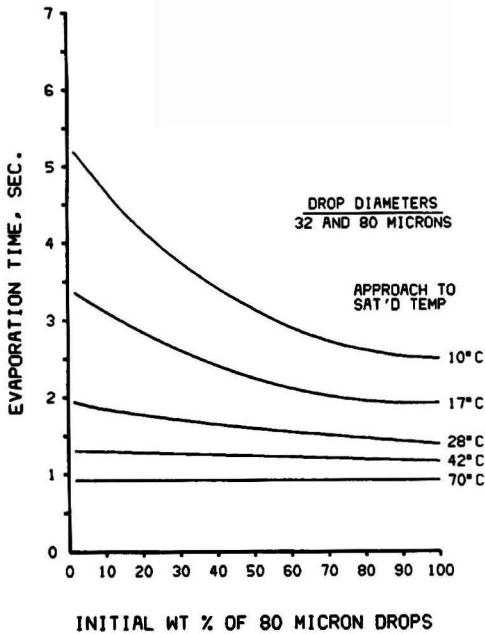


Figure 2. Evaporation Times (Maximum Drop Diameter Equals 80 Microns).

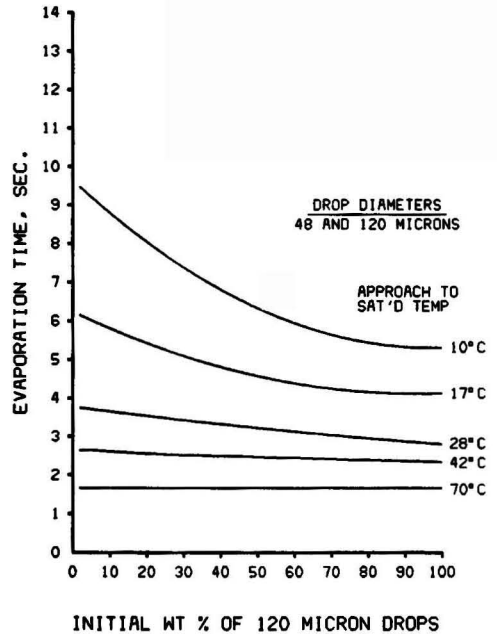


Figure 4. Evaporation Times (Maximum Drop Diameter Equals 120 Microns).

small because both sizes of smaller drops rapidly consume the driving force.

Using the discreet drop size distribution given in Table 1, the model was used to compute the evaporation times for several approaches to saturation. Table 4 shows the computed evaporation times can be estimated by using Figure 2 with the assumption that the largest 2% of the drops are 80 microns in diameter. If a given distribution

does not have a maximum drop size close to the 80, 100 or 120 microns it is possible to crossplot the data on Figures 2, 3, and 4 at a fixed approach to adiabatic saturation and weight percent of maximum drops. This crossplot gives a curve of evaporation time versus maximum drop diameter for the specific case.

The curves on Figure 2, 3, and 4 were computed from the model based on flue gas flowing in a horizontal duct. Computations of the evaporation time for the gas flowing horizontal, vertically down and vertically up shown in Table 5, indicate that the effect of orientation is minimal. Had the drops been larger or the gas velocities lower, the influence of orientation would be significant.

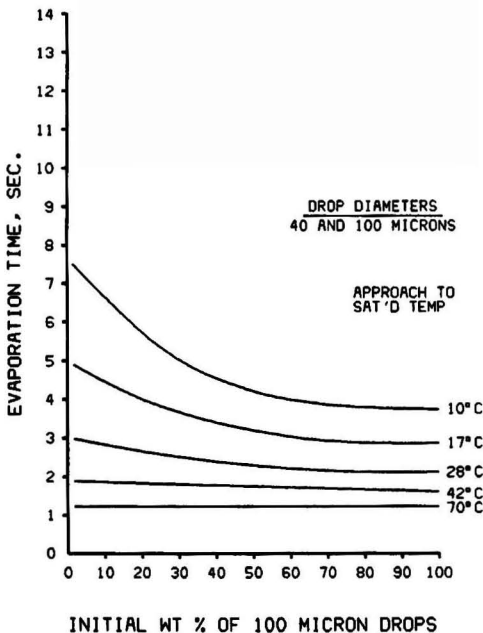


Figure 3. Evaporation Times (Maximum Drop Diameter Equals 100 Microns).

Length of the Humidification Section

The model also computes the length of the humidification chamber for each specific condition. An estimate of the length of the humidification chamber can be made from knowing the inlet flue gas rate, the inlet and outlet flue gas temperatures and the evaporation time. From the flue gas conditions an average gas velocity can be computed and multiplied by the evaporation time to estimate the required length for humidification. Table 6 shows that estimated duct length are within 5% of the lengths computed with the model.

COSTS OF A HUMIDIFICATION SYSTEM

Both the capital and operating costs of a humidification system are dependent on the quantity of water to be evaporated and the size of the maximum drops in the distribution produced by the nozzle. The amount of water required depends on the gas flow rate and the approach to adiabatic saturation. The maximum size drop that could be used without wetting the duct depends on the approach to adiabatic saturation and the residence time in the duct available for evaporation. Drop size measurements provided by nozzle manufacturers and measure-

TABLE 3. EVAPORATION TIMES OF TWO DROP SIZE DISTRIBUTIONS

Drop Distribution	Evaporation
1. 75%, 40 micron diameter 25%, 100 micron diameter	2.65 sec.
2. 75%, 25 micron diameter 25%, 100 micron diameter	2.72 sec.

TABLE 4. EVAPORATION TIMES FOR THE DROP DISTRIBUTION GIVEN IN TABLE 1.

Approach to Adiabatic Saturation Temperature, °C	Evaporation Time, Sec. Computed	Est. From Fig. 3*
10	8.10	7.5
17	5.04	4.9
28	2.90	3.0
42	2.02	2.0
70	1.23	1.2

* Estimated at 2 wt. % of drops equal to 100 microns.

TABLE 5. EVAPORATION TIMES FOR HORIZONTAL, UPFLOW AND DOWNFLOW GAS FLOWS

Flow Direction	Time For Evaporation (Seconds)
Horizontal	2.33
Upflow	2.48
Downflow	2.26

Conditions

- 1) Gas cooled to 28°C from adiabatic saturation.
- 2) Drop distribution is 50 wt. % 40 micron drops and 50 wt. % 100 micron drops.
- 3) Other conditions see Table 2.

TABLE 6. LENGTH OF DUCT REQUIRED FOR HUMIDIFICATION

Approach to Adiabatic Saturation Temperature of Humidified Gas	Evaporation Time, Sec.	Required Duct Length, M.	
		Estimated	Computed
17	4.9	45.6	44.2
28	3.0	28.4	27.3
42	2.0	18.5	17.6

Conditions

- 1) As given in Table 2

ments taken at an independent research laboratory [5] show that increasing the air to water ratio results in a decrease in the drop size. Table 7 lists the approximate air consumption required to achieve a maximum size drop for nozzles with operating ranges of 550 to 2200 kg/hr (0.5 to 2.0 gpm).

Table 8 lists the primary capital cost items of a humidification system installed on a 100 megawatt boiler. The minimum duct modifications include ports and internal supports for installation of the nozzles. The total capital cost greatly depends on whether or not duct modifications are necessary. The largest operating cost for the system is the compressor power required by the atomization air. Figure 5 shows the power requirements expressed as a

TABLE 7. AIR REQUIREMENTS OF TWO-FLUID NOZZLES

Air Requirements Nm ³ /Liter Water	Air Requirements (SCF/Gal. Water)	Maximum Drop Diameter (Microns)
.354	50	80
.283	40	100
.212	30	120

Conditions

- 1) Air pressure at nozzle inlet = 552 kPa (80 PSIA)

TABLE 8. ESTIMATED PURCHASE COSTS OF EQUIPMENT COMPONENTS FOR AN IN-DUCT HUMIDIFICATION SYSTEM FOR A 100 MW BOILER

Component	Estimated Purchase Cost
1. 4 Compressors (including 1 spare)	\$130,000
2. 70, Nozzles	\$3,500
3. 10, Nozzles manifolds	\$30,000
4. Pressure gauges and flow meters	\$40,000
5. Piping	\$30,000 and up
6. Duct modifications	\$20,000 and up

Conditions

- 1) Gas humidified to 28°C from adiabatic saturation temperature.

percent of the output of the boiler. These computations assumed the air consumption produced 80 micron drops (see Table 7). If larger drops could be used (i.e. longer duct lengths are available) then the air consumption would be reduced and result in a proportional decrease in power consumption.

CONCLUSIONS

1. The evaporation time required for a distribution of drops is always larger than if all the drops were at the maximum size.

The ratio of the evaporation time for a given distribution to the evaporation time of a distribution with all the

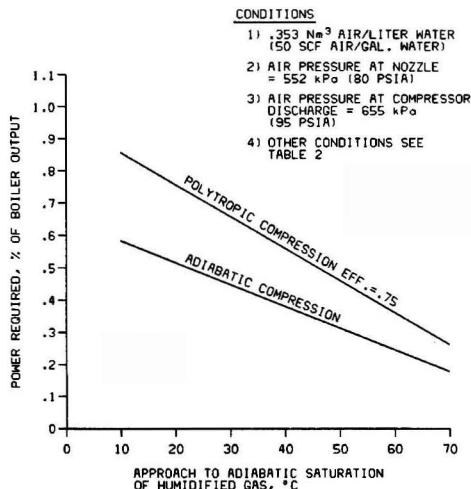


Figure 5. Power Requirement for atomization air.

drops equal to the maximum size rapidly increases as the approach to saturation increases.

The evaporation time required to achieve a specified approach to the adiabatic saturation temperature of the outlet flue gas will decrease if the maximum drop size is decreased.

The evaporation time for drop distributions of two-fluid nozzles used to humidify a typical utility flue gas upstream of an ESP can be estimated by assuming the distribution consists of only two sizes where the larger drop diameters equal the average of the drops that comprise the largest .5 to 1 weight % of the actual distribution and that the other diameter is equal to 40% of the larger diameter.

The ratio of the mass of atomization air to mass of water increases as the required maximum diameter of the drop size decreases; therefore, the power requirements for the compressed air increases.

The capital cost of a humidification system is small compared to the power requirements, providing no duct modifications are required to provide the necessary time for evaporation of the water drops.

APPENDIX

Outline of Method for Computation of the Evaporation Time

The model for computing the evaporation time of a dispersion of drops performs computations during the two phases of the life of the drops. The first phase, designated as Region #1, is the heating up of the initial drops from their inlet temperature (usually ambient) to the adiabatic saturation of the drops. The model performs heat and material balances on each individual discrete drop size over fixed increments of length. At the end of each increment of length the model computes the total amount of heat transferred to all the drops and then computes a new gas temperature. Computations are repeated in the next increment of length until the next of the specified duct length is reached or all the water evaporates.

The amount of heat transferred to a single drop over an increment of time is given by the expression:

$$Q = \pi h D^2 (T_g - T_d) \quad (1)$$

The heat coefficient is given by Ranz and Marshall's (5):

$$Nu = 2(1 + 0.3 Pr^{1/3} Re^{1/2}) \quad (2)$$

The Reynolds number in Equation (2) is based on the relative velocity of the drop and surrounding gas. A force balance on the drops can be expressed as

$$dU/dt = -.75 C V^2 \rho_g / D \rho_w + Kg (1 - (\rho_g / \rho_w)) \quad (3)$$

where U is the absolute drop velocity and V is the relative velocity of the drop and the gas given by

$$V = U - U_C \quad (4)$$

The constant K in Equation (3) is zero for horizontal flow, +1 for cocurrent downflow, and -1 for cocurrent upflow. The drag coefficient, C, is also evaluated at the Reynolds number based on relative drop velocity. For the drops size and velocities for the humidification of flue gas

the drag coefficient is usually in the transition or Stokes' Law region of flow.

The computations are started in Region #1 by specifying a small fixed length and computing the time it takes each drop size to transport over that distance by numerically solving Equation (3). The average relative velocity for each drop size over the increment is computed and then the amount of heat transferred to each drop size is computed from Equations 1 and 2. This permits computation of a new drop temperature and a new gas temperature. The model assumes that the gas is completely mixed at the end of each increment. If the computations had been in Region #2, instead of computing a new drop temperature, the amount of water evaporated would be computed. The computations are repeated for each increment until the largest drops have completely evaporated or the end of the humidification section has been reached.

NOTATION

C	drag coefficient
D	drop size
g	acceleration by gravity
K	constant in Equation 3
Nu	Nusselt Number
Pr	Prandtl Number
Q	heat transfer to drop
Re	Reynolds Number
t	time
T _g	temperature of bulk gas
T _d	temperature of drop
U	absolute drop velocity
U _C	gas velocity
V	relative velocity defined by Equation 4
π	3.1416
ρ _a	gas density
ρ _w	water density

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Catalytic Oxidation of Groundwater Stripping Emissions

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Air stripping has been shown to be an efficient and cost effective method of removing volatile organic contaminants from groundwater and soil. The removal of dissolved fuel fractions and chlorinated solvents at efficiencies in excess of 95% has been demonstrated on several occasions. Unfortunately, these contaminants are transferred to the air where they may continue to pose an environmental and health threat. Regulation of such emissions has already been considered in many states including Michigan and California. However, few options are available for their control. Vapor phase carbon adsorption and thermal incineration are the two treatment methods which have been applied most often. These technologies have some disadvantages. Adsorption merely transfers the contaminant to a solid phase, which in turn requires disposal or regeneration. Thermal incineration may be expensive, since it requires a substantial energy input to destroy dilute gas phase contaminants. A new alternative is appearing in the form of catalytic oxidation. Like thermal incineration, it is an ultimate disposal method, but since it operates at much lower temperatures, the energy costs are also lower. This paper reviews the applicability of catalytic oxidation to control groundwater air stripping gaseous effluents with special attention given to system designs and case histories. The variety of contaminants and catalyst poisons encountered in stripping operations are also reviewed.

INTRODUCTION

The catalytic oxidation of volatile substances such as methanol and ammonia over platinum was observed in the nineteenth century, and has become a major industrial process during the twentieth century. The subject of catalytic oxidation has been thoroughly reviewed by various authors including Golodets [1], Prasad *et al.* [2], and Margolis [3]. Most of the work reviewed is that of industrial interest. This work falls into roughly two categories: (1) partial oxidation for the manufacture of petrochemicals such as ethylene oxide, maleic anhydride, and acetylaldehyde; and (2) deep oxidation of contaminants in air for emissions control such as found in automotive catalysts. A recent review by Spivey [4] covers the application of catalytic oxidation to dilute organic contaminant streams. There have been no papers to date specifically

concerned with catalytic control of emissions from air stripping units, and only two actual applications of this technology in the field have been documented.

A hypothetical system with catalytic destruction of air stripping effluents is pictured in Figure 1. Air is countercurrently contacted with a contaminated water stream. Most volatile compounds are transferred to the air stream, and the water receives a final cleanup in the liquid polishing step before disposal. The catalytic destruction of organic emissions in the air stream differs from other catalytic pollution control applications in several important aspects. First, the concentration of the contaminants in the gas phase is quite low, in most cases less than 100 ppmv. Second, the humidity levels are unusually high since the air stream is saturated coming off the stripping unit. Third, a wide variety of contaminants and mixtures ranging from chlorinated compounds and soluble fuel

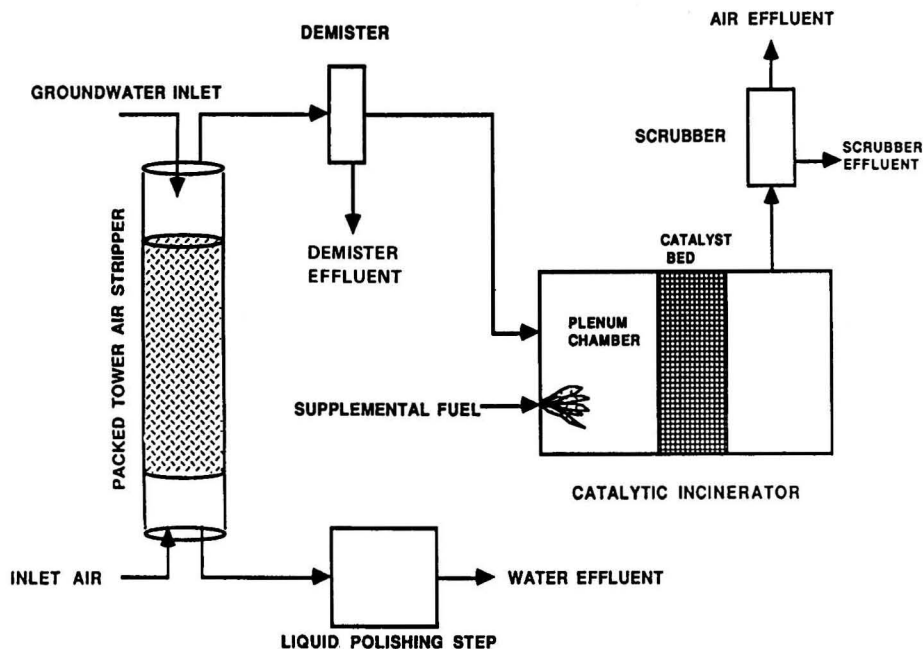


Figure 1. System configuration for catalytic destruction of air stripping emissions.

fractions to pesticides and polychlorinated biphenyls may be in any groundwater source. Finally, the water vapor stream exiting a groundwater stripper may have high concentrations of mineral aerosols and poisons (e.g., hydrogen sulfide) that will shorten catalyst life. All of these factors make the design and implementation of catalytic treatment uncertain. Some of these uncertainties are to be considered here, in addition to industrial resources and system economics.

FUNDAMENTALS FOR SYSTEM DESIGN

The majority of catalytic oxidation processes have been developed for the production of oxidized chemical feedstocks such as sulfuric acid, maleic anhydride, and ethylene oxide. In the case of petrochemical feedstocks, the oxidation process is carefully controlled to prevent the reaction from producing the most thermodynamically favored products, carbon dioxide and water. Only in a few cases, most notably automobile emission control systems, is the process designed to promote complete (deep) oxidation of the reactants. In addition, the concentration of reactants in industrial catalytic processes is usually in the percent range; whereas, for contaminant control, the reactant concentrations are very low, usually less than 100 ppmv (0.01%). More specifically, the emissions from air stripping units may consist of a complex mixture of reactants including both fuel and solvent fractions. A typical example of an air stripping off gas stream is shown in Table 1. This table lists the concentration of selected contaminants emitted from a pilot air stripping unit at Wurtsmith Air Force Base in Michigan (Stallings *et al.* [5]). Here, no individual contaminant exceeds 70 ppmv, but the cumulative total exceeds 170 ppmv. These concentrations are in the range of those seen by automotive catalysts; however, automotive catalyst units cannot be directly compared, because they are also designed to simultaneously accomplish the oxidation of carbon monox-

ide and the reduction of oxides of nitrogen.

Even though the oxidation reactions in both cases are highly exothermic, the concentrations of reactants from an air stripper are far too low to supply the heat necessary to raise the catalyst bed temperature. Usually, this temperature must be high enough to provide a practical reaction rate for destruction. Figure 2 shows the effect of catalyst operating temperature on the rate of oxidation. The rate of oxidation initially increases exponentially with temperature, and then levels off as mass transfer of reactants to the catalyst surface becomes the rate limiting factor. At still higher temperatures, the reaction no longer relies solely on the surface reaction, and the region of catalytically supported combustion dominates. In the case of automotive catalysts, the exit gases from the engine are sufficiently hot to provide this energy, but the air

TABLE 1. TYPICAL ORGANIC CONCENTRATIONS IN AIR STRIPPING OVERHEAD [5]

Compound	Concentration in gas phase (ppmv)*
Pentane	42.4
Cyclohexane	66.1
Methyl cyclopentane	7.7
2,3-Dimethyl butane	1.6
Trichloroethylene	17.9
Benzene	9.2
Ethyl benzene	8.3
Cumene	3.4
Mixed xylenes	21.3
Total	177.9

*Calculated at a gas/liquid ratio of 42/1 for 1-in. (2.5-cm) Pall rings.

from stripping units is usually near groundwater temperatures, approximately 5° to 25°C. This is far below the operating temperatures of available oxidation catalysts; therefore, heat must be provided in the form of an electric heater or fuel fired burner. To promote energy savings, one would ideally desire the temperatures to be the minimum at which the desired destruction efficiency can be accomplished. This usually corresponds to the mass diffusion controlled regime in Figure 2.

The energy burden of heating a cold, water-laden air stripping effluent stream should be lower for a catalyst system than for thermal incineration, but it still represents a considerable operating cost. The air from most air stripping units can be considered to be saturated with water (100% relative humidity). This corresponds to an absolute water vapor concentration of between 0.8 and 3.1% in the exit stream. The action of bubbles in the stripping unit also produces a large amount of liquid aerosol. The carryover of liquid water in the form of small droplets and aerosol represents an additional large heat burden on any catalyst bed and should be minimized by the use of demisters or filters if possible. Aerosol removal has an additional advantage, in that mineral or biological matter which might foul and deactivate the catalyst bed is also removed.

The high concentration of water vapor in the effluent stream represents a major difference between this application of catalytic control and others which have been previously investigated. Hence, the effect of high humidity on the catalytic chemistry of hydrocarbon oxidation and the destruction of other contaminants has not been previously ascertained. The oxidation of hydrocarbons is generally thought to occur via a surface redox cycle known as the Mars-van Krevelan mechanism (Golodets [1]). This mechanism results in a rate expression of the form:

$$r = \frac{k_{O_2} k_{HC} C_{O_2} C_{HC}}{k_{O_2} C_{O_2} + \gamma k_{HC} C_{HC}}$$

Here k_{O_2} is the rate constant for catalyst surface oxidation, k_{HC} is the rate constant at which the hydrocarbon reduces the oxidized surface, C_{O_2} and C_{HC} are the respective concentrations of oxygen and hydrocarbon, and γ is the stoichiometric requirement of oxygen necessary to completely convert the hydrocarbon to water and carbon

dioxide. A multicomponent form of this equation has also been developed by Gangwal *et al.* [6]. The products of reaction do not appear in this rate expression, but Golodets [1] has postulated that water and carbon dioxide can inhibit the reaction by competitively adsorbing on reaction sites. Preliminary experimental studies by the authors on the effect of humidity on catalytic oxidation of hydrocarbons indicate that this inhibition effect is minimal for most hydrocarbons in fuel fractions. However, for compounds which may hydrolyze (*e.g.*, ethyl acetate), water may actually enhance the oxidation rate. As of now, however, no firm basis exists to predict the behavior of hydrocarbon oxidation in the presence of water.

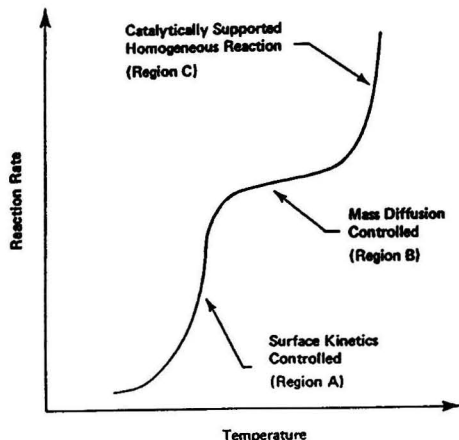
The effect of water on the catalytic destruction of chlorinated compounds is generally thought to be beneficial. The most easily treated products of this process are hydrochloric acid (HCl), carbon dioxide, and water; however, some solvents such as trichloroethylene (C_2HCl_3) do not have stoichiometric amounts of hydrogen to allow complete reaction of the chlorine to HCl. For those compounds, water may serve as this hydrogen source, or may merely favorably alter the reaction thermodynamics. Other hydrogen sources such as methane or propane may also be beneficial in promoting HCl formation. As with the non-halogenated hydrocarbons, a clearer understanding of the catalytic chemistry is essential to understanding the role of water vapor.

As a further complication, many contaminated groundwater sources may contain mixtures of hydrocarbons and halogenated compounds. Gangwal *et al.* [6] and Tichenor and Palazzolo [7] have found significant mixture effects for oxidation of hydrocarbons, chiefly in the form of inhibition. This means that catalytic oxidation of a given compound is generally negatively impacted by the presence of mixtures, and higher catalyst bed operating temperatures may be necessary to achieve adequate destruction. To date, information on mixture effects for halogenated compounds is extremely limited, although Doronina [8] and others in the Russian literature report successful catalytic treatment of organic and halogenated compound mixtures.

Catalysts exposed to air stripping effluent are subject to deactivation from several sources—fouling, thermal degradation, poisoning, and catalyst volatilization. Due to dissolved salts and mineral matter in the off gases from the stripping operation, the catalyst bed may plug or become encrusted and lose effectiveness. As mentioned previously, removal of aerosols prior to the catalyst unit may alleviate this problem. If the catalyst bed is operated at high temperatures (>600°C) for prolonged periods, sintering of active noble metals may occur also resulting in loss of activity. Groundwater also often contains significant amounts of readily strippable compounds, such as hydrogen sulfide (H_2S), that may poison the catalyst surface by adsorbing and blocking active sites. Higher operating temperatures may remove some of these poisons, but sintering may then become a problem. Finally, some reactants, especially halogenated compounds, may chemically bond with the active catalyst and subsequently volatilize from the surface. The loss of catalyst associated with this vaporization process inevitably results in lower catalyst efficiency.

CATALYTIC UNITS FOR CONTAMINANT REMOVAL

Ideally, to accomplish the catalytic deep oxidation of contaminants, a highly active, non-selective catalyst is desired. The compositions of commercial catalysts for deep oxidation are generally proprietary in nature, but generally consist of low weight loadings of platinum or palladium (0.1 to 3%) on metal or metal oxide substrates.



After: Prasad *et al.* [2].

Figure 2. Reaction regimes for catalytic oxidation.

Sometimes the noble metals are supplemented by a base metal component or a metal oxide wash coat on the support. For application to halogenated compounds, metal oxides of compounds such as copper, vanadium, or chromium may show superior resistance to deactivation. The large body of literature on the formulation and chemistry of oxidation catalysts cannot be adequately summarized here, but reviews by Golodets [1], Spivey [4], and others provide an introduction to the subject.

A catalyst with high activity at low temperatures is desirable, but enough heat must be supplied to effect complete destruction. However, extremely high temperatures (>750°C) may actually produce more partial reaction products. Basically, this means that a minimum operating temperature of at least 350°C should be employed with catalysts currently available. To attain these temperatures, most catalyst units, regardless of the catalyst bed structure, use a preheating unit. This preheater may be electric or an open flame type. The open flame type is generally powered by natural gas or propane, and may accomplish a significant degree of destruction by itself (Tichenor and Palazzolo [7]). These preheaters are used with most of the reactors now available commercially, in both fixed and fluidized bed designs.

There are several commercial catalytic units now on the market in this country, and many others in Europe. To our knowledge, however, there is experience with only two of these in conjunction with an air stripping unit. Most of these units are now used for controlling emissions from solvent stripping operations, paint spray booths, and similar industrial operations where concentrations of reactants are much higher. Several of the commercially available catalytic incinerators have been identified and are described below:

1. **ARI:** This fluidized bed catalytic incinerator was a new development in the early 1970s. Developed jointly by Air Resources, Inc. and Harshaw Chemical Company, this technology has been in commercial use since 1975 and is being marketed on a turnkey basis (Hardison and Dowd [9]). The catalyst, developed by Harshaw Chemical Company, is a nonprecious metal disposable pellet. The fluidized design is especially good in that it overcomes carbon fouling (masking) problems. The moving catalyst bed allows masked catalyst to move to higher temperature zones in the bed, thereby oxidizing the masking material. Approximately 50 of these fluidized bed units are being used for volatile organic compound (VOC) control. Of the 50, a significant portion are used for control of chlorinated hydrocarbons.

ARI and Union Carbide have recently cooperated to develop a new system employing ARI fluidized bed catalyst technology and Union Carbide molecular sieve adsorbent expertise. Their system uses Silicalite adsorbent to preconcentrate organic emissions before they are fed to the catalytic unit. The combined system is said to be more cost effective than catalytic destruction alone since the catalytic unit can be downscaled by a factor of 10 or more.

2. **CE Air Preheater:** CE markets both thermal and catalytic incinerator systems in sizes ranging from 3,400 to over 170,000 m³/hr. Their catalyst, supplied by Johnson-Matthey, is platinum deposited on a stainless steel honeycomb. CE Air Preheater had installed 17 catalytic incinerator systems as of 1988.
3. **Dedert Corporation:** Dedert markets a "CATOX" catalytic incinerator for Haldor Topsoe A/S, a Danish company specializing in catalysts. It features a non-noble metal catalyst resistant to chlorine, sulfur, and phosphorus compounds in both

monolith and pellet form. They market a special ADOX unit for low concentrations (<250 ppmv), and another, named REGENOX, for "dirty" streams. Many of these units are in place for manufacturing and industrial processes.

4. **Engelhard (Torvex):** Since the early 1980s, this system has been marketed by the Engelhard Corporation. Complete systems are available in sizes ranging from less than 1,700 to 120,000 m³/hr. Their catalysts consist of precious metal deposited on ceramic honeycombs. Between 1976 and 1988, the vendor supplied about 250 complete catalytic incinerator systems in the U.S. and over 1000 in Japan and retrofitted about 200 thermal incinerators with catalyst.
5. **Groundwater Technology, Inc.:** Groundwater Technology provides complete groundwater cleanup services. As such, they have entered the area of cleanup of air emissions from these operations. They report installation of their first catalytic conversion unit. The catalyst was obtained from Johnson-Matthey and consists of platinum on a metal substrate. Effective destruction of fuel mixtures stripped from groundwater has been cited [10].
6. **Johnson-Matthey:** A major manufacturer of catalysts and other materials employing precious metals markets a variety of self contained catalyst treatment systems for removal of organic compounds from gaseous effluents. Their Honeycat unit may be fitted with either a ceramic or metal honeycomb catalyst support. Inexpensive units are marketed for treatment of low volume streams.
7. **Met-Pro Corporation:** Formerly Oxy-Catalyst, this company markets both thermal and catalytic incineration systems and carbon adsorption systems. They employ a wide range of catalysts including both precious and nonprecious metals deposited on a monolithic or pellet support. They have installed over 200 catalytic incinerator systems throughout the United States and some foreign countries (Kenson [11]).
8. **TEC Systems:** This producer manufactures and markets catalytic incinerator systems that utilize a granular catalyst bed. These incinerators have been effectively used to control VOC emissions from a number of industrial processes.
9. **Ultrax:** Ultrax International continues to develop and market a system based on a combined ultraviolet (UV)/ozone/catalytic oxidation technology. When used for water treatment, the groundwater contaminated with chlorinated hydrocarbons is pumped into a reaction tank where an ozone/air mixture is bubbled through the water. This bath is simultaneously irradiated with UV light. In addition to the oxidation in the aqueous phase, a portion of the hydrocarbons are stripped from the water and pass into a UV/catalytic reactor where further oxidation occurs at temperatures slightly above ambient.

CASE STUDIES

The U.S. Environmental Protection Agency (EPA), during the past several years, has sponsored or co-sponsored several evaluations of catalytic control devices. During 1984, a Torvex unit from Engelhard Corporation was evaluated using low concentrations of several compounds (Tichenor and Palazzolo [7]). The objectives were to investigate the effects of operating and design variables on destruction efficiency in mixtures of contaminants. Tests showed that destruction efficiencies exceed-

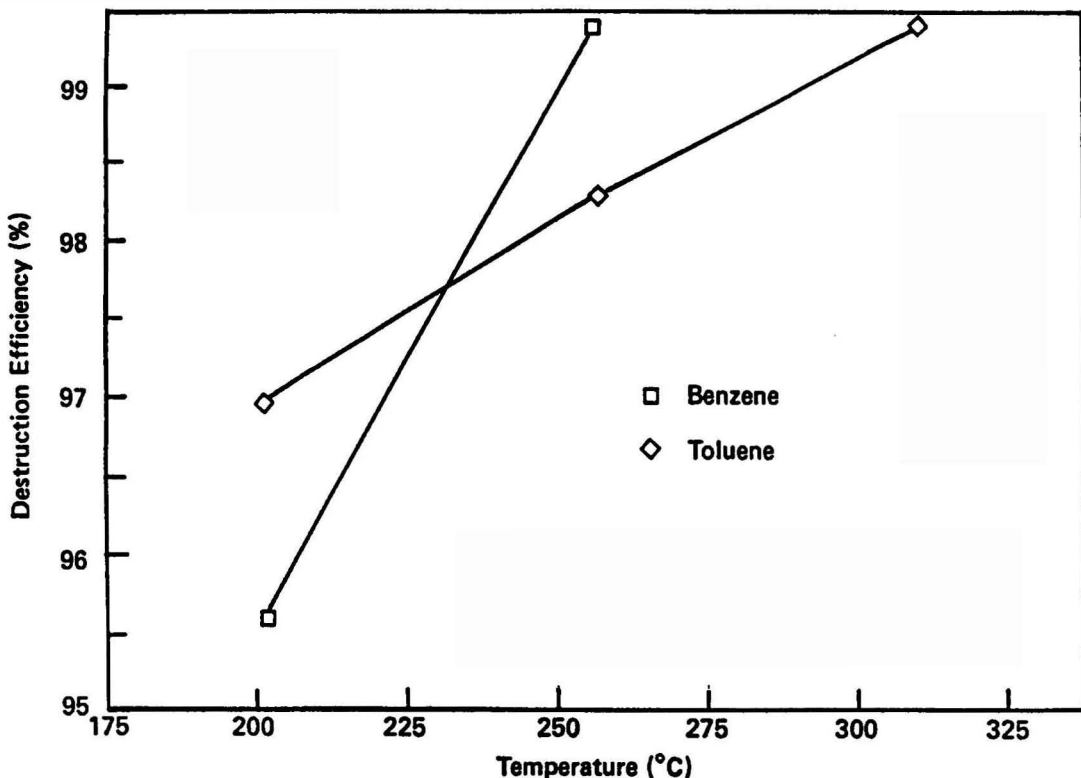


Figure 3. Destruction efficiency of a pilot scale catalytic incinerator for benzene and toluene in air stripper exhaust. [13]

ing 95% could be attained for alcohols, acetates, ketones, aldehydes, aromatics, and ethylene oxide. Chlorinated compounds were not effectively destroyed with this catalyst.

The EPA and the U.S. Air Force Engineering and Services Center cooperated to evaluate other off-the-shelf technologies including the fluidized bed unit from ARI and the UV/ozone/catalytic unit from Ultrox (Palazzolo *et al.* [12]). For the Ultrox unit, the destruction of chlorinated compound mixtures was evaluated with both ozone addition and UV light. It was found that destruction efficiencies without ozone addition in the presence of UV light were low. The presence or absence of UV light with ozone addition did not have a significant effect on destruction efficiency, which was 99% in either case. However, unidentified by-products were actually being formed in the presence of ozone which lowered overall destruction efficiency to approximately 75%.

A recent EPA report [13] identified 177 air strippers in the United States. Of these, 17 are equipped with air emission controls. Of the 17 facilities, 1 uses a catalytic incinerator, 2 have open flares, 2 have thermal incinerators, and 12 have granular-activated carbon adsorbers. Installation of the air control device was required by the governing state at nine of these sites.

The catalytic incinerator identified in that study is located at the U.S. Coast Guard Base in Traverse City, Michigan. This air stripper system began operation in 1985. The catalytic incinerator was included in the initial design and installation of the air stripping system. The air stripper installed at this site is a rotary high-gravity air stripper which achieves high removal efficiencies at lower air to water ratios than packed towers. The lower

air flow for this type of air stripper results in higher pollutant concentrations in the air stripper exhaust. The catalytic incinerator at Traverse City was installed for destruction of benzene, toluene, and xylene stripped from the groundwater. The catalytic oxidation unit is designed for a flow of 3,400 m³/hr and operates at 260° to 320°C. The design efficiency for this catalytic incinerator was 90%; however, no performance data are yet available.

The performance of catalytic incinerators has been demonstrated for control of organic air emissions from air stripping of groundwater in one other case [13]. The destruction performance achieved during pilot scale testing of an air stripper exhaust stream containing benzene and toluene is presented graphically in Figure 3. The incoming air from the stripping unit contained less than 10 ppm total organics. It can be readily perceived from the lack of performance data on field systems that a large portion of research in this area remains to be conducted.

SYSTEM ECONOMICS

Two recent studies have evaluated the cost of control technologies for air emissions from groundwater stripping. The first of these was completed for EPA's Control Technology Center (CTC) in August 1987 [13]. Here the costs for the Traverse City site are estimated. Installed cost for the catalytic unit is \$198,500, and annual operating costs for the 3,400 m³/hr unit are \$95,920 (third quarter 1986). This report also estimates control costs and efficiencies for carbon adsorption and thermal incineration for four other air stripper sites. Table 2 summarizes these estimates. It may be noticed from this table that the an-

TABLE 2. SUMMARY OF AIR STRIPPING EXHAUST CONTROL SYSTEMS [13]

	Site A	Site B	Verona Well Field	Plainfield
Contaminants	Trichloroethylene (4,000)	Chloroform (1,500)	Ethylene dichloride (5)	Perchloroethylene (200)
Concentration (ppbw)	Trichloroethane (300)		Trichloroethane (12) Dichloroethylene (10) Trichloroethylene (1) Perchloroethylene (10)	
Water Flowrate (lpm)	5,300	590	7,200	13,600
Air Flowrate (Nm ³ /hr)	13,600	2,200	9,400	32,600
Organic Removal Efficiency (%)	99	99.9	99.9	99.6
Control Options:				
Carbon Adsorption				
Control efficiency (%)	~80	not reported	74	90
Installed cost (\$)	150,000	152,000	223,000	500,000
Direct operating cost (\$)	50,400	31,300	62,700	120,000
Total annualized cost (\$)	96,400	77,800	124,000	221,000
Thermal Incineration				
Control efficiency (%)	98	98	98	98
Installed cost (\$)	318,000	187,000	285,000	432,000
Direct operating cost (\$)	432,000	86,800	303,000	1,047,000
Total annualized cost (\$)	492,000	129,000	358,000	1,123,000
Catalytic Oxidation				
Control efficiency (%)	95	95	95	95
Installed cost (\$)	307,000	134,000	251,000	586,000
Direct operating cost (\$)	210,000	51,600	150,000	508,000
Total annualized cost (\$)	269,000	86,100	201,000	606,000

nualized costs of control increase as a function of air flow rate for all of the systems. The most rapid increase in cost is for thermal incineration, with catalytic oxidation being twice as cost effective for the 32,600 m³/hr unit. This emphasizes the energy savings mentioned previously for catalytic systems. Carbon adsorption still has a more favorable operating cost; however, for the operating systems considered in the CTC report, the expected control efficiencies for thermal and catalytic incineration (>95%) were much greater than the observed efficiencies for adsorption (70 to 90%). Of course, carbon adsorption can attain higher control efficiencies with increased bed size or decreased relative humidity of the emission stream. However, such changes will result in increased capital and annualized operating costs. A cost analysis for an existing high efficiency (>95%) carbon adsorption system is not presently available. The tradeoffs between control efficiency and costs must be made in light of the nature of the contamination threat.

In a second report, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) recently published a study comparing the economic viability of several control technologies for air emissions from groundwater stripping and soil purging operations [14]. The objective of this study was to identify those emerging technologies which could be competitive with traditional controls. Among the options considered were the fluidized bed incinerator of ARI, the UV/ozone/catalytic oxidation unit from Ultrox, the PURASIV fluidized carbon adsorption system of Union Carbide, and the KPR/incinerator system marketed in the United States by Met-Pro. This last unit uses an activated carbon fiber adsorbent and special equipment to preconcentrate contaminant fumes prior to incineration. For 1 year of operation for a 1,400 to 12,000 m³/hr unit, catalytic oxidation and carbon adsorption were the most cost competitive. UV/ozone and thermal incineration became less cost effective as flowrates increased; and the PURASIV and KPR processes were almost twice as expensive per year as standard carbon adsorption at all

flowrates examined. The final recommendation of the report was to pursue a demonstration of a fluidized bed catalytic oxidation unit.

CONCLUSION

Catalytic destruction of groundwater air stripping emissions is an attractive technology in that: (1) the contaminants are destroyed, not simply transferred to another phase; (2) destruction efficiencies in excess of 95% are readily attained; (3) it represents a cost effective alternative to other technologies available; and (4) commercial units are currently available for use. Unfortunately, aside from one limited study, there exists no experimental database on which to quantitatively evaluate this approach. Control of emissions from air stripping units differs from other similar applications because of the low concentrations of contaminants, the high humidity, and catalyst deactivation mechanisms. Laboratory scale experiments to understand the chemistry of reaction for different contaminant types and to evaluate catalyst formulations and activities will play an important role in removing technical uncertainties. Matching of catalyst to contaminant, selection of reactor type and operating temperatures, and development of techniques to realistically evaluate performance will greatly aid transfer of the technology to the field.

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Removal of Pollutants from Dilute Wastewater by the PACT™ Treatment Process

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The PACT™ wastewater treatment system, which incorporates the use of powdered activated carbon in a conventional activated sludge system, has been in use for the treatment of wastewaters from both municipal and industrial sources. The combination of physical adsorption with biological oxidation and assimilation in the PACT system has been shown to be particularly effective in treating dilute wastewaters which are variable in concentration and composition, highly colored, or contain materials which are refractive or potentially toxic to biological growth.

Dilute wastewaters treated successfully in bench-scale PACT systems include those from organic chemicals, pharmaceuticals, metal coating, shale oil retort water, evaporation ponds, leachates, and rainwater runoff. The COD of these wastewaters ranged from a low of 643 mg/l to 23,700 mg/l. Specific pollutants present included compounds such as phenols, cyanides, thiocyanate, pesticides, and priority pollutants. The PACT wastewater treatment process has successfully treated these wastewaters and produced effluents meeting POTW or direct environmental discharge requirements.

Operational parameters and performance results obtained for a number of bench-scale PACT systems are presented.

INTRODUCTION

Modern technology can produce wastewaters that present difficult treatment problems. These wastewaters are often highly variable in composition and contain substances which are difficult to degrade biologically or even toxic to the microorganisms employed in the treatment process. The addition of powdered activated carbon to an activated sludge system provides a process, known as the PACT treatment system, which can meet the challenge of these difficult to treat wastewaters.

Description of the System

The PACT wastewater treatment system consists of the addition of powdered activated carbon to the aeration basin of a biological activated sludge system. This combination of physical adsorption with biological oxidation and assimilation has been shown to be particularly effective in treating wastewaters which are variable in concentration and composition, highly colored, or contain materials which are potentially toxic to biological growth. Characteristic advantages of the PACT wastewater treatment system over conventional activated sludge are:

1. Improved BOD and COD removals.

2. Stability of operation with variability in influent concentration and composition.
3. Enhanced removal of toxic substances and priority pollutants.
4. Effective color removal.
5. Improved solids settling.
6. Suppressed stripping of volatile organics.

The PACT wastewater treatment system operates in accordance with the flow diagram shown in Figure 1. Influent wastewater flows to the aeration tank where the wastewater is mixed with powdered activated carbon and biological solids. The wastewater-carbon-biological solids mixture is aerated for a sufficient hydraulic detention time to achieve biological oxidation and assimilation of the biodegradable content of the wastewater. After aeration, the mixture flows to a clarifier where the powdered carbon and biological solids are settled and separated from the treated wastewater. The clarifier overflow (treated wastewater) is discharged from the PACT system. The clarifier underflow solids are returned to the aeration tank on a continuous basis to maintain a desired concentration of powdered activated carbon and biological solids.

A portion of the biological solids and spent powdered activated carbon is wasted daily from the PACT system. Virgin powdered activated carbon addition is therefore required to maintain the desired aeration basis carbon concentration. The addition rate of virgin carbon is deter-

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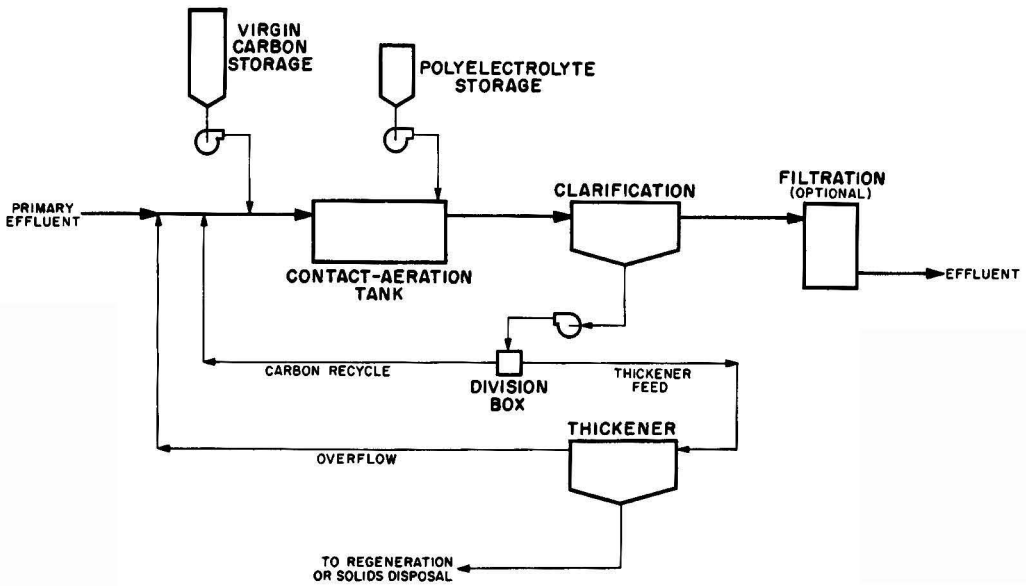


Figure 1. PACT wastewater treatment system general process diagram.

mined by treatment requirements, waste load and wastewater characteristics.

Operation of the PACT system is controlled by adjustment of specific process parameters. These parameters are:

1. Hydraulic Detention Time (HDT)
2. Solids Residence Time (SRT)

3. Carbon Mixed Liquor Suspended Solids (CMLSS)
4. Carbon Dose (CD).

In operating the PACT system, selection of initial process conditions is usually made based on knowledge of the characteristics of the waste to be treated, the desired treatment results (effluent quality), and past experiences with the application of the PACT system.

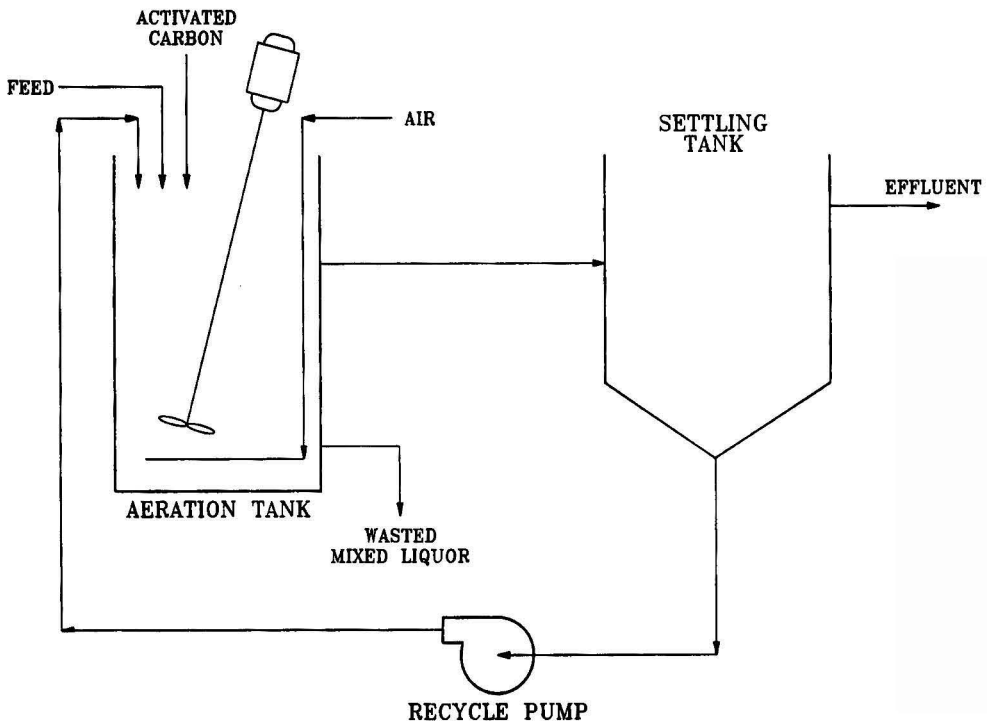


Figure 2. Laboratory scale PACT system.

BENCH-SCALE PACT SYSTEM DESCRIPTION

Bench-scale treatability studies are routinely performed at Zimpro/Passavant Inc. to evaluate treatment of various wastewaters with the PACT system. Wastewaters are typically treated in bench-scale continuous-flow PACT systems as shown in Figure 2. The major components of the bench-scale systems include 2.0 to 4.0 liter cylindrical aeration tanks with mechanical mixers, external conical clarifiers, and peristaltic feed and mixed liquor recycle pumps. Mixed liquor dissolved oxygen (D.O.) levels are maintained above 2.0 ppm using air diffusers located at the bottom of the aeration tanks.

The bench-scale systems are initially seeded with waste activated sludge from a municipal wastewater treatment plant and a wastewater grade powdered activated carbon. Feed to the PACT system is initially a mixture of wastewater and municipal primary effluent. The PACT system is normally acclimated to the full-strength wastewater by gradually increasing the fraction of wastewater in the feed mixture to 100 percent over a several week period. Micro- and macro-nutrients are added to the raw wastewater if a nutrient deficiency exists.

Daily operation of the PACT system includes measuring feed and effluent volumes and mixed liquor pH, D.O. and oxygen uptake rates (O.U.R.). Mixed liquor is wasted directly from the aeration basin on a daily basis in order to maintain the desired solids residence time (SRT). The desired carbon dose rate is provided by adding powdered activated carbon to the aeration basin on a daily basis.

PACT SYSTEM PERFORMANCE RESULTS

Numerous bench-scale PACT system treatability studies have been performed on various wastewater streams

at Zimpro/Passavant, Inc., over the past several years. Performance results obtained during nine of these bench-scale PACT system treatability studies are presented and discussed in the following sections. The studies selected were chosen to represent the diversity of wastewaters which are readily treatable by the PACT system.

The PACT system treatability studies presented were typically performed over a two to three month period and usually included two or more steady state treatment periods of 20 to 30 days each. The data presented in the following sections generally represent performance results obtained during one steady state operating period for each study.

As would be expected for the diverse nature of the wastewaters treated, treatment objectives varied from study to study. In some cases, pretreatment to meet POTW discharge standards was required, while others required treatment to a level suitable for direct environmental discharge. For a number of studies, the major objective was carbonaceous removal only, whereas both carbonaceous removal and nitrification was required in some instances.

Performance results for several studies were based on conventional wastewater parameters only such as chemical oxygen demand (COD), biochemical oxygen demand (BOD₅) and dissolved organic carbon (DOC). In others, specific pollutants were monitored routinely or periodically throughout the study including priority pollutants, pesticides, phenols, cyanide and thiocyanate.

The following studies illustrate the variety of dilute wastewaters which have been shown to be treatable by the PACT wastewater treatment system.

Study A. In Study A, pond water from a commercial hazardous waste disposal facility was treated in a laboratory-scale PACT system. The raw wastewater consisted of a variety of chemical production wastewaters which were

TABLE I. STUDY A: TREATMENT OF POND WATER BY THE PACT™ SYSTEM

Operating Conditions:			
HDT	2.3 days		
SRT	5.8 days		
Carbon Dose	2270 mg/l		
Treatment Performance:			
	Influent	Effluent	Percent Removal
COD, mg/l	11,780	1580	86.6
BOD ₅ , mg/l	5150	16	99.7
DOC, mg/l	2470	362	85.3
(1) Priority Pollutant Volatile Fraction:			
Benzene	290	<1	>99.7
Carbon Tetrachloride	860	<1	>99.9
Chloroform	1470	<1	>99.9
1,1-Dichloroethane	640	<1	>99.8
1,2-Dichloroethane	210	<1	>99.5
Dichloromethane	29,700	5.8	99.98
Ethylbenzene	185	<1	>99.5
Tetrachloroethylene	304	<1	>99.7
Toluene	2730	<1	>99.9
1,1,1-Trichloroethane	4970	<1	>99.9
Trichloroethylene	326	<1	>99.7
(1) Priority Pollutant Acid Fraction:			
Phenol	2400	<2	>99.9
(1) Priority Pollutant Base-Neutral Fraction:			
Butylbenzyl Phthalate	129	<2	>98.4
Bis(2-Ethylhexyl) Fthalate	561	<2	>99.6
Diethylphthalate	88	<1	>98.9
Dimethylphthalate	332	<1	>99.7
Isophorone	1490	37	97.5
Napthalene	191	<1	>99.5

(1) Units in µg/l.
< Values represent detection limits.

combined in evaporation ponds for treatment prior to landfill disposal of the residual solids.

The raw pond water was a relatively high strength wastewater having COD and BOD₅ concentrations of 11,780 and 5150 mg/l, respectively. The pond water also contained high concentrations of many organic priority pollutant compounds. The PACT system achieved very effective treatment of the pond water as shown by the performance results listed in Table 1. Effluent generated during treatment averaged 1580 mg/l COD and 16 mg/l BOD₅, corresponding to 86.6 percent COD removal and 99.7 percent BOD₅ removal.

The PACT system was especially effective in removal of the organic priority pollutants contained in the pond water. Priority pollutants identified in the pond water at concentrations above 1000 µg/l included chloroform, dichloromethane, toluene, 1,1,1-trichloroethane, phenol and isophorone. A number of priority pollutants were present at lower concentrations as well. The PACT system achieved 99.98 percent removal of dichloromethane and 97.5 percent removal of isophorone. Effluent concentrations were 5.8 µg/l for dichloromethane and 37 µg/l for isophorone. All other priority pollutants identified in the pond water were reduced to below detection limits by the PACT system.

Study B. A bench-scale PACT system was used to demonstrate treatment of a spent solvent wastewater in Study B. The spent solvent wastewater was initially pretreated

in a full-scale wet air oxidation (WAO) system, which accomplished significant destruction of the bulk of organic pollutants contained in the waste. The wet air oxidized product was subsequently treated in a bench-scale PACT system with the results shown in Table 2.

The PACT system achieved excellent treatment of the oxidized solvent wastewater as shown by overall removals of 94.5 percent for COD, >99.8 percent for BOD₅, 98.9 percent for nonpurgeable organic carbon (NPOC), and 96.6 percent for color. Corresponding effluent concentrations for these parameters were 390 mg/l COD, <8 mg/l BOD₅, 25 mg/l NPOC and 20 APHA color units.

In addition to the excellent treatment of conventional wastewater parameters, the PACT system was also shown to achieve excellent removals of residual organic compounds remaining in the solvent wastewater after wet air oxidation. Only trace amounts of methyl acetate, methyl ethyl ketone, ethanol and 1,1,1-trichloroethane were detected in the PACT system effluent with all other compounds reduced to nondetectable levels.

Samples of PACT system influent and effluent were also analyzed in this study for toxicity using the Microtox[®] Toxicity Analyzer. Results of this testing showed the PACT system achieved a 40+ fold reduction in toxicity. The treated effluent showed no toxicity to the bacteria used in the Microtox[®] test (5 min. EC₅₀ = >100 percent), compared to a 5 min. EC₅₀ of 2.4 percent for the influent wastewater.

TABLE 2. STUDY B: TREATMENT OF SPENT SOLVENT WASTEWATER BY THE PACT[™] SYSTEM

Operating Conditions:			
HDT	3.8 days		
SRT	20.0 days		
Carbon Dose	850 mg/l		
Treatment Performance:			
	Influent ⁽¹⁾	Effluent	Percent Removal
COD, mg/l	7140	390	94.5
BOD ₅ , mg/l	5250	<8	>99.8
NPOC, mg/l	2330	25	98.9
Color, APHA units	580	20	96.6
⁽²⁾ Specific Organic Compounds:			
Isobutyl Acetate	14	<5	>64
Acetaldehyde	8900	<20	>99.78
1,1,1,2-Tetrachloroethane	36	<10	>72
Methanol	208,000	<10	>99.99
Acetonitrile	30,000	<30	>99.9
Methylene Chloride	84	<20	>76
Acetone	233	<20	>91
Isopropanol	224	<60	>73
Methyl Acetate	14,000	74	99.47
Tetrahydrofuran	130	<10	>92
Methyl Ethyl Ketone	2300	14	99.39
Ethanol	16,000	146	99.09
m-Xylene	33	<10	>70
o-Xylene	79	<5	>94
1,2-Dichlorobenzene	30	<5	>83
Benzene	29	<5	>83
Carbon Tetrachloride	2000	<30	>98.5
Chlorobenzene	31	<5	>84
Chloroform	38	<20	>47
Dichlorobromomethane	500	<20	>96
Dichloropropene	36	<5	>86
Ethylbenzene	21	<5	>76
Tetrachloroethylene	136	<10	>93
Toluene	57	<5	>91
1,1,1-Trichloroethane	405	25	93.8
1,1,2-Trichloroethane	30	<5	>83
Trichloroethylene	90	<10	>89

< Values represent minimum detection limits.

(1) Wastewater was pretreated by wet air oxidation prior to PACT system treatment.

(2) Units in µg/l.

Study C. In Study C, a bench-scale PACT system was used to demonstrate treatment of a pesticide-containing wastewater generated at an agricultural chemicals production facility. The raw wastewater treated in this study contained significant concentrations of various organophosphorus, organochlorine and carbamate pesticides. The raw wastewater was also very high in COD (9110 mg/l), BOD₅ (750 mg/l) and DOC (1690 mg/l).

The combined biological treatment and carbon adsorption of the PACT system proved very effective in treating the pesticide wastewater (see Table 3). COD, BOD₅ and DOC reductions of 99.0, 97.6, and 98.6 percent, respectively, were achieved by the PACT system. The organophosphorus pesticide dimethoate was reduced by 85.9 percent to an effluent concentration of 180 µg/l during PACT treatment. All other pesticides present in the raw wastewater were reduced by 99.7 percent and

higher by the PACT system with the majority of the pesticides reduced to nondetectable levels.

Study D. A shale oil retort wastewater derived from a pilot-scale synthetic fuels production facility was treated in Study D. Included in Study D was a parallel conventional activated sludge bench-scale system operated at conditions equivalent to the PACT system.

The shale oil retort wastewater was very high strength having COD, BOD₅ and DOC concentrations of 23,700, 6220 and 4950 mg/l, respectively. Specific components present in the wastewater included high concentrations of phenols (71.4 mg/l), cyanide (60.1 mg/l) and thiocyanate (191.7 mg/l).

Results achieved during treatment of the shale oil retort wastewater by the PACT and activated sludge systems are shown in Table 4. The PACT system achieved a high degree of treatment of the raw wastewater with 89.4 per-

TABLE 3. STUDY C: TREATMENT OF PESTICIDE PRODUCTION WASTEWATER BY THE PACT™ SYSTEM

Operating Conditions:				
HDT		4.3 days		
SRT		10.0 days		
Carbon Dose		8600 mg/l		
Treatment Performance:		Influent	Effluent	Percent Removal
COD, mg/l		9110	93	99.0
BOD ₅ , mg/l		750	18	97.6
DOC, mg/l		1690	24	98.6
⁽¹⁾ Organophosphorus Pesticides:				
Diazinon		4480	<0.05	>99.9
Dimethoate		1280	180	85.9
Cythion (Malathion)		12,000	<0.05	>99.99
Forate (Thimet)		540	<0.05	>99.99
Ethyl Parathion		1000	<0.05	>99.99
Ethion		4400	<0.05	>99.99
⁽²⁾ Organochlorine Pesticides:				
β-BHC		104	0.31	99.70
Endosulfan I		10,000	1.04	99.99
Endosulfan II		3000	<0.05	>99.99
Lindane		860	0.47	99.95
⁽¹⁾ Carbamate Pesticides:				
Carbaryl		600	<2.0	>99.67
Methiocarb		7200	5.0	99.93

(1) Units in µg/l.

< Values represent detection limits.

TABLE 4. STUDY D: TREATMENT OF SHALE OIL RETORT WASTEWATER BY PACT™ AND ACTIVATED SLUDGE SYSTEMS

Operating Conditions:	Activated Sludge System			
	PACT System	Activated Sludge System		
HDT, days	5.0	4.9		
SRT, days	9.4	9.0		
Carbon Dose, mg/l	4260	—		
Treatment Performance:		PACT System Effluent	Activated Sludge System Effluent	
COD, mg/l		23,700	2510	8430
Percent Removal		—	89.4	64.4
BOD ₅ , mg/l		6220	27	650
Percent Removal		—	99.6	89.5
DOC, mg/l		4950	840	2990
Percent Removal		—	83.2	39.6
Phenols, mg/l		71.4	0.20	2.88
Percent Removal		—	99.7	96.0
Cyanide, mg/l		60.1	0.65	39.3
Percent Removal		—	98.8	34.6
Thiocyanate, mg/l		191.7	16.2	229.6
Percent Removal		—	91.5	—

TABLE 5. STUDY E: TREATMENT OF METAL COATING WASTEWATER BY THE PACT™ SYSTEM

Operating Conditions:			
HDT	4.2 days		
SRT	19.3 days		
Carbon Dose	1140 mg/l		
(1) Treatment Performance:	Influent	Effluent	Percent Removal
COD	11,510	186	98.4
BOD ₅	3990	18	99.5
DOC	2490	39	98.4
Methanol	20	<1	>95.0
Ethanol	504	<1	>99.8
Methyl Ethyl Ketone	266	<1	>99.6
N-Butanol	62	<1	>98.4
Butyl Carbitol	2,950	<1	>99.9
Triethyl Amine	222	1.5	99.3

(1) Units in mg/l.
< Values represent detection limits.

cent COD reduction, 99.6 percent BOD₅ reduction and 83.2 percent DOC reduction. In addition, the PACT system achieved excellent phenols (99.7 percent), cyanide (98.8 percent) and thiocyanate (91.5 percent) removals.

In contrast, results for the activated sludge system showed only moderate treatment of the shale oil retort wastewater. COD, BOD₅ and DOC removals for the activated sludge system were 64.4, 89.5 and 39.6 percent, respectively. The activated sludge system achieved reasonable phenols removal (96.0 percent) but was ineffective in removing cyanide (34.6 percent) and thiocyanate (0.0 percent).

Study E. A wastewater generated as part of a metal coating line process was treated in Study E using a bench-scale PACT system. The metal coating line wastewater was very high strength and also contained high concentrations of a number of organic chemicals used in coating line operations. Performance results obtained during Study E are shown in Table 5.

The PACT system demonstrated excellent treatment of the metal coating line wastewater with COD, BOD₅ and DOC reductions of 98.4, 99.5 and 98.4 percent, respectively. In addition, analyses of the specific organic chemicals contained in the wastewater showed triethyl amine was reduced by 99.3 percent to an effluent concentration of 1.5 mg/l. All other compounds measured in the raw wastewater were reduced to below detection limits of 1 mg/l by the PACT system.

Study F. A second metal coating line wastewater was treated in Study F. This wastewater was similar to that evaluated in Study E, being very high strength and containing a number of metal coating line chemicals.

As shown in Table 6, excellent treatment of the second metal coating line wastewater was obtained during PACT treatment. Effluent generated by the bench-scale PACT system had an average COD of only 81 mg/l and BOD₅ of <6 mg/l. Corresponding removals were 99.4 percent for COD and >99.8 percent for BOD₅. In addition, all coating line chemicals monitored during the study were reduced to nondetectable levels by the PACT system.

Study G. The PACT system has been shown to be a highly effective process for treatment of landfill leachates. In Study G, landfill leachate from a National Priority List landfill site was treated using a bench-scale PACT system. In this study, the raw leachate was also spiked with high concentrations of the chlorinated organic compounds trichloroethylene (TCE), 1,4-dichlorobenzene (1,4-DCB) and 2-chlorophenol (2-CP).

Performance results obtained during PACT treatment of the spiked leachate are shown in Table 7. The results show that chlorinated organic removal efficiencies of essentially 100 percent were achieved at feed concentrations as high as 101.3 mg/l total TCE, 1,4-DCB and 2-CP. Throughout the study period, all three chlorinated organic compounds remained undetected in the PACT system effluent.

PACT system aeration basin offgases were also monitored during the study to determine the extent of TCE and 1,4-DCB removal due to volatilization during treatment. Results of the offgas sampling showed only minimal losses of TCE (0.12 percent or less) and 1,4-DCB (1.17 percent or less) due to volatilization, thus confirming the ability of the PACT system to suppress stripping of volatile compounds during treatment.

In addition, excellent carbonaceous removals and nitrification performance were demonstrated during PACT treatment of the spiked leachate. Even at chlorinated organic addition levels in excess of 100 mg/l, COD, BOD₅ and DOC removals of 93.5, >99.5 and 94.0 percent, respectively, were achieved. Ammonia nitrogen (NH₃-N) concentrations were reduced by nearly 99 percent as well.

Study H. In Study H, a synthetic wastewater representative of a pharmaceutical production wastewater was treated using a bench-scale PACT system. The synthetic wastewater was high strength and also contained high levels of NH₃-N at 590 mg/l.

As shown in Table 8, the PACT system achieved 93.7 percent COD reduction, >98.9 percent BOD₅ reduction,

TABLE 6. STUDY F: TREATMENT OF METAL COATING LINE WASTEWATER BY THE PACT™ SYSTEM

Operating Conditions:			
HDT	4.2 days		
SRT	14.8 days		
Carbon Dose	1910 mg/l		
(1) Treatment Performance:	Influent	Effluent	Percent Removal
COD	13,620	81	99.4
BOD ₅	3680	<6	>99.8
Isopropanol	400	<4	>99.0
Methyl Ethyl Ketone	300	<0.01	>99.9
N-Butanol	1,200	<1	>99.9
2-Ethylhexanol	250	<5	>98.0
Dimethylethanolamine	350	<8	>99.7
Propylene Glycol Methyl Ether	2,800	<3	>99.9

(1) Units in mg/l.
< Values represent detection limits.

TABLE 7. STUDY G: TREATMENT OF LANDFILL LEACHATE BY THE PACT™ SYSTEM

Operating Conditions:

HDT	1.0 days
SRT	11.2 days
Carbon Dose	2420 mg/l

(1) Treatment Performance:

	Influent	Effluent	Percent Removal
COD	2950	191	93.5
BOD	1538	<8	>99.5
DOC	926	56	94.0
NH ₃ -N	142	1.5	98.9
Trichloroethylene	32.8	<0.005	>99.98
1,4-Dichlorobenzene	36.6	<0.015	>99.96
2-Chlorophenol	31.9	<0.05	>99.84

(1) Units in mg/l.
 < Values represent detection limits for chlorinated organic compounds.

TABLE 8. STUDY H: TREATMENT OF PHARMACEUTICAL PRODUCTION WASTEWATER BY THE PACT™ SYSTEM

Operating Conditions:

HDT	5.3 days
SRT	31.7 days
Carbon Dose	2440 mg/l

(1) Treatment Performance:

	Influent	Effluent	Percent Removal
COD	6020	380	93.7
BOD ₅	3210	<36	>98.9
DOC	2760	59	97.9
NH ₃ -N	590	18	96.9

(1) Units in mg/l.

TABLE 9. STUDY I: TREATMENT OF RAINWATER RUNOFF BY THE PACT™ SYSTEM

Operating Conditions:

HDT	1.1 days
SRT	8.3 days
Carbon Dose	940 mg/l

(1) Treatment Performance:

	Influent	Effluent	Percent Removal
COD	643	14	97.8
BOD ₅	182	<6	>96.7
DOC	118	4	96.6

(1) Units in mg/l.

and 97.9 percent DOC reduction during treatment of the synthetic pharmaceutical production wastewater. In addition, the PACT system achieved a high level of nitrification with NH₃-N reduced by 96.9 percent to an effluent concentration of 18 mg/l.

Study I. A bench-scale system was used to demonstrate PACT treatment of contaminated surface runoff waters from a chemical terminal facility. Treatment results obtained by the PACT system during Study I are shown in Table 9.

The PACT™ system proved to be a very effective treatment process for the surface runoff wastewater. The PACT system achieved 97.8 percent COD removal, >96.7 percent BOD₅ removal and 96.6 percent DOC removal. This level of treatment produced a highly treated effluent having only 14 mg/l COD, <6 mg/l BOD₅ and 4 mg/l DOC.

CONCLUSION

Numerous bench-scale treatability studies have demonstrated the ability of the PACT wastewater treatment system to treat a wide variety of dilute wastewaters. The PACT system is capable of achieving high levels of overall treatment and has been shown to be particularly effective for removal of specific pollutants including organic priority pollutants, pesticides, phenols, cyanide and thiocyanate.

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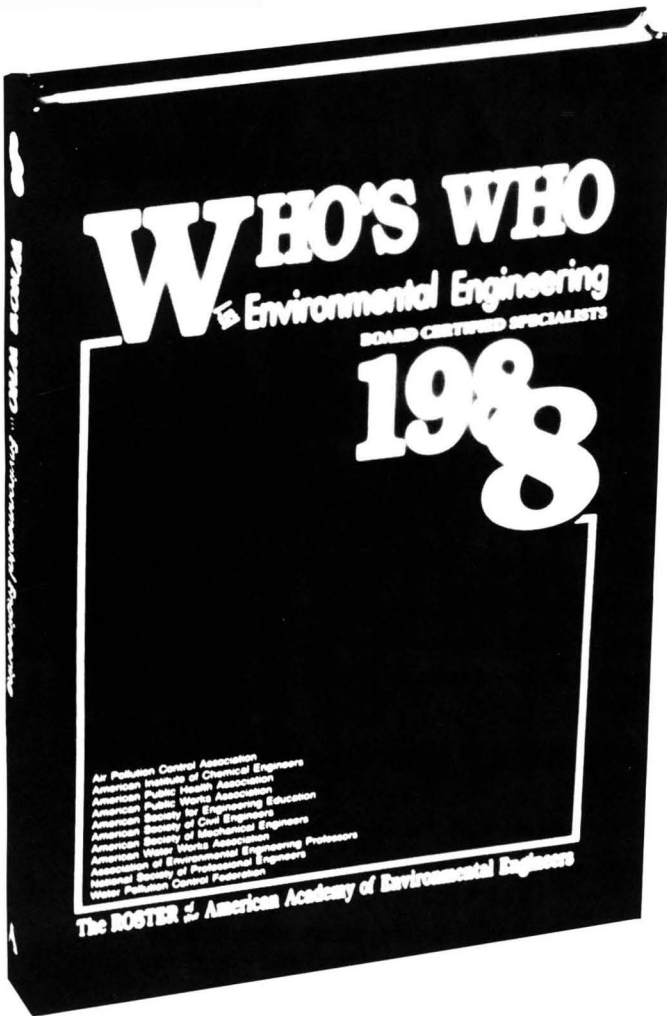
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