ENVIRONMENTAL PROGRESS

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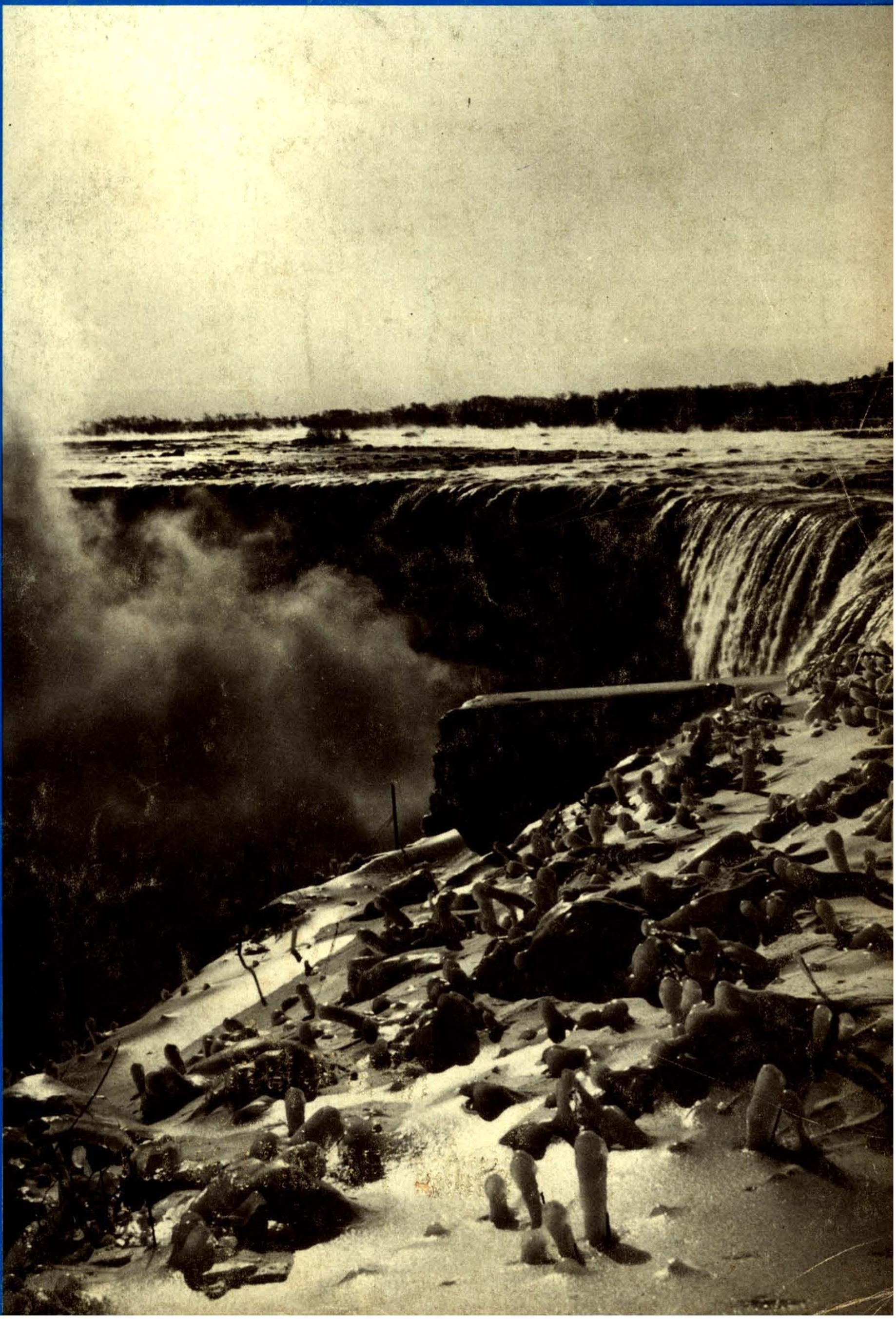

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PROGRESS

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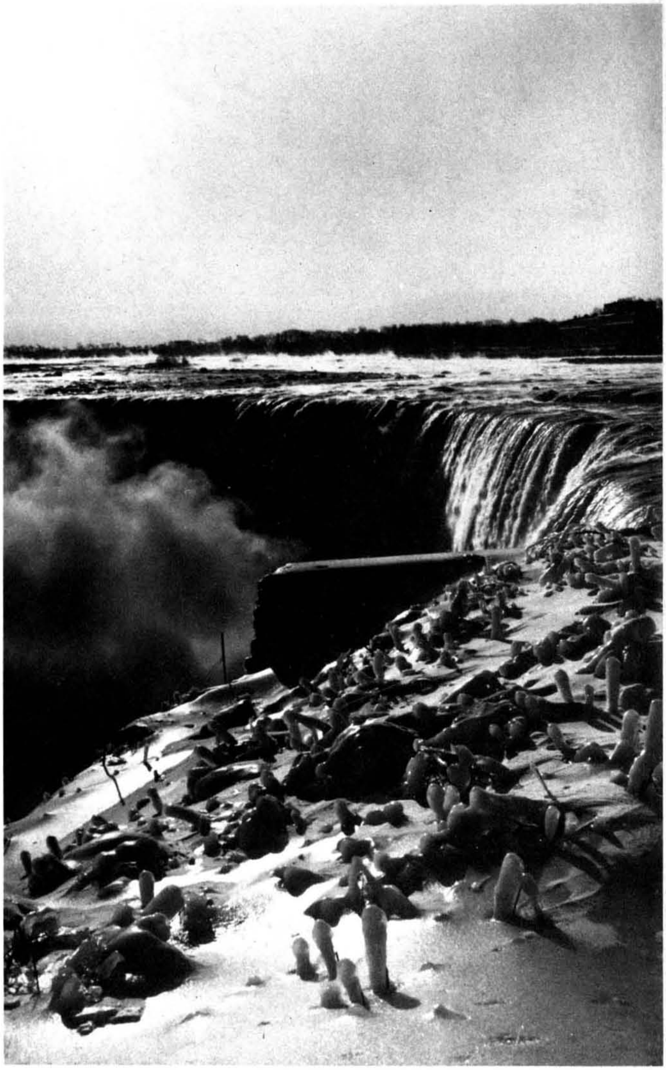

Dawn over Horseshoe Falls.
Photo courtesy Niagara Falls Convention & Visitors Bureau.

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There is a tide in the affairs of men . . .

Shakespeare
Julius Caesar, Act 4, Sc. 3.

While returning from the 11th International Conference of the IAWPR, in Cape Town, South Africa, I had a good bit of time for thinking. One thing that kept popping up in my mind was: what is going to be the future of water pollution control in the U.S. and how are the members of the Environment Division going to be involved in it?

I thought back to the early days of our active involvement with the government on water pollution control, and how our work led to the very effective program of the AIChE GPSC. We of the Environmental Division, without anything other than moral support from the GPSC and AIChE, prepared and submitted testimony before the National Commission on Water Quality for Amending the Federal Water Pollution Control Act.

At that time we were in the forefront of change, the cutting edge of the development of new legislation and regulations. We were the first professional society to recommend that the municipal construction grants program be terminated. This is the program under which the federal government pays seventy-five percent of the cost of engineering, design and construction of municipal sanitary sewage treatment and facilities, and collection systems. We were later followed by the American Water Works Association. And recently even such organizations as the Water Pollution Control Federation have seen fit to get on the bandwagon that we started moving.

Our reasons for this position was that the construction grants program was not effective as a pollution control program. It was a public works program pure and simple, and it should have been viewed as such. In fact, it soon became crystal clear that we were correct, and not only was the program ineffective for pollution control, but rather it probably did more to impede the cleanup of the water of the nation than any other single factor or program. It had a strong, negative impact.

In looking at programs today and what is needed, now with the construction grants program expected to be gradually phased out, there will seemingly be less money available for municipal sewage treatment plant construction. What program then could we come up with that would lessen the need for larger (and "better") sanitary sewage treatment plants. And here we come to what I expect will be the controversial part of what I have to say.

I recommend that we in the Environmental Division see what can be done to *encourage industry to divert out of municipal sewage treatment systems all wastes that cannot be beneficially treated by biological treatment methods.* For this to happen to any degree there are a number of things that will have to come about.

First, the regulatory agencies (federal, state and local) will have to be brought on board. The regulatory agencies must monitor the permitted outfalls in their area and the fewer outfalls there are, the less work they have to do. Thus, it has been their attitude in the past to encourage industries to pretreat their waste and then if possible to discharge it through a municipal sewage treatment system. I maintain that this is neither cost effective nor is it environmentally sound. Properly treated industrial wastewater that cannot be beneficially treated by biological systems, should be discharged directly to the surface waters. If discharged to a municipal sanitary sewage treatment system the minimum effect it will have is to increase the hydraulic load on the system, and consequently, the total pounds of BOD which the plant will discharge into the environment.

Second, we will have to convince industry that this is in their best interest also. I think that in many cases this will be somewhat easier, particularly if industry is to be required to pay its fair share of construction and operation costs for municipal treatment systems. With many industrial discharges now requiring pretreatment before discharge into the municipal sanitary system, would it not be better to allow these properly pretreated wastes to be discharged directly to the surface waters.

In many cases this will also require changes of piping systems within the industrial plant so that wastes that can be beneficially treated by biological methods can be kept separate from those which cannot. Changing of piping within a plant can be very expensive. But over the long run, if we start now on working toward this system, doing the educating necessary, and creating the proper atmosphere, we will be moving ahead toward the type of environment that we have all been working for, and we will be doing it in a most cost effective manner.

I realize that there may be a substantial amount of opposition to this proposal. There will be individual plants where this will not work today. And for the plants that are so small that pretreatment is not required, this system may not work. But my experience in metals finishing in plants located in large cities or in small towns, is that this system will work, and it will be cost effective, and environmentally sound.

Let's be the leaders again and get this new concept moving down the road.

T. H. GOODGAME

T. H. Goodgame is a member of the advisory board of *Environmental Progress,* Past Chairman of the Environmental Division and Past Director of AIChE. He holds a Ph.D in chemical engineering and is Environmental Control Director of Whirlpool Corp., Benton Harbor, MI.

PRESENTS

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Environmental Shorts. . .

Battelle to Study Environmental Effects of Drilling on Large Commercial Fishing Area

A study to identify the environmental effects of drilling exploration on the Georges Bank is being conducted by Battelle's New England Marine Research Laboratory, Duxbury, MA for the U.S. Department of Interior, Bureau of Land Management.

Georges Bank, located southeast of the MA coast, supports one of the largest commercial marine fisheries in the world. In recent years, however, alternative uses for the Bank have been proposed, including offshore drilling for oil and natural gas.

According to a Battelle spokesman, there have been concerns that these alternative uses of the Bank could seriously damage the fishing industry.

Exploratory drilling began in the area in July 1981. Drilling fluids—or muds—often are discharged in small quantities during the exploration. These water-based fluids contain the mineral, barite, and small quantities of clay and other materials.

The major emphasis of this research and monitoring program will be to determine short and long-term changes in the bottom-living fauna that can be attributed to oil and gas exploration. If harmful effects are detected, corrective measures can be taken by the oil industry or the government.

New Lab Test Will Help Assess Relative Toxicity of Burning Materials

Researchers at the U.S. Commerce Department's National Bureau of Standards (NBS) have developed and published a test method that will help to assess the relative toxicity of materials when they burn.

Product manufacturers, building officials, and others who want to know more about the toxicity of the combustion products of various materials have been handicapped by the lack of an agreed upon laboratory test. The bureau's suggested test method, published in a report released today, will provide laboratories with a method for evaluating materials of concern.

The NBS test involves heating a sample material in a special furnace and exposing test animals (rats) to the combustion products. The materials are tested under both flaming and non-flaming conditions in an attempt to reflect two major modes of material decomposition in fires.

The procedure calls for animals to be exposed to the combustion atmosphere for 30 minutes, a time chosen as representative of the escape or rescue time for an occupant of a burning building. The animals are then monitored for 14 days following exposure, reflecting the situation in which fire victims die some time after escape. Death of 50 percent of the test animals during the test or post-exposure period determines the lethal concentration of a burning material. The test also provides an optional procedure to examine materials which rapidly produce combustion products during a 10 minute exposure. In addition, the NBS test method describes analytical and physiological measurements which can provide more detailed information and will be helpful in determining the need for further research on specific materials.

Copies of the NBS reports, *Further Development of a Test Method for the Assessment of the Acute Inhalation Toxicity of Combustion Products*, which describes the test method, notes refinements over an earlier version, and lists results from illustrative tests on sample materials, will be available in several weeks from the National Technical Information Service.

EPA Publishes Guide on Clean Efficient Operation of Boilers

The U.S. Environmental Protection Agency has published a guide on clean and efficient operation of coal stoker-fired boilers.

The 72-page guide, prepared by EPA's Industrial Environmental Research Laboratory (IERL) Research Triangle Park, NC. and designed for use by boiler operators, explains and illustrates the types of coal-fired stokers, the combustion process, and reasons for heat loss and inefficiency.

It goes on to discuss ways in which coal stoker-fired boilers can be operated at peak efficiency and with minimum pollutant emissions. Step-by-step instructions are included.

Copies of the publication, titled "A Guide to Clean and Efficient Operation of Coal Stoker-Fired Boilers," are available for $9.00 from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161. Ask for publication #EPA-600/8-81-016. Copies will also be available for $25.00 through the American Boiler Manufacturers Association, 950 North Glebe Road, Suite 160, Arlington, VA. 22203.

New hazard communication system presented to OSHA

With its Hazardous Materials Identification System (HMIS), the paint and coatings industry has developed a simple, easy-to-use and effective hazard communication system which may eventually be adaptable for use by workers in other industries.

Testifying at the recent Occupational Safety and Health Administration (OSHA) hearing in Washington, D.C., on its proposed hazard communication standard for chemical industry workers, National Paint and Coatings Association (NPCA) member representatives from DeSoto, Inc. and the Grow Group, Inc., described the HMIS system, which uses numerical and pictorial codes to inform workers of work place materials hazards and appropriate protective equipment.

Permanganate solves odor and corrosion problems in pulp and paper industry

Recent tests by Carus Chemical Co., La Salle, IL, have disclosed that use of potassium permanganate is successful in controlling the problems caused by sulfide compounds at pulp and paper plants.

Already used widely by municipal wastewater treatment plants to eliminate obnoxious odors, Cairox potassium permanganate has been found effective in oxidizing unwanted sulfides in the mill wastewater. The tests were conducted at both pulp and paper mills in WI.

Hydrogen sulfide (H_2S) gas can react with oxygen in the air to form acids in the atmosphere. In addition to this corrosive atmosphere, the hydrogen sulfide odor is highly objectionable and can be toxic.

A spokesman for Carus Chemical, identified three major benefits of using potassium permanganate in wastewater treatment:

1. improved health and safety for plant employees,
2. control of corrosion to extend equipment life, and
3. elimination of obnoxious and toxic hydrogen sulfide odors as a good-neighbor policy.

Further information is available from the Technical Services Department, Carus Chemical Co., La Salle, IL.

LETTERS

More on "Prediction of Destruction Efficiencies"

To the editor:

Mr. Brown's letter [*Environmental Progress*, 1, M7 (1982)] about my paper [*Environmental Progress*, 1, 38-42 (1982)] asked for "some correction" to be published. I assume he was referring to the fact that E can be different for different temperature ranges (due to changing mechanisms). Though not stated explicitly in the paper, the empirical A and E values used must be derived for temperature ranges of interest.

Currently, the most directly applicable data from the laboratory for empirical pseudo first order rates of disappearance is that being generated by thermal destruction units. These units normally operate up to about 1200°K (1700°F), well within the lower range of boiler firebox temperatures.

The model is designed to give an upper bound on the amount of emitted material, not the actual value. In this light, using lower rate constants is appropriate. Using pyrolitic rates (i.e., those generated in nitrogen) is the safest approach, but normally lead to criticisms of "over conservatism."

The question of turbulence is addressed by starting the calculations at the point of maximum average bulk gas temperature. This point occurs slightly beyond the point of maximum heat release rate. The rate of heat release is primarily a function of oxygen concentration and fuel concentration within an elemental reaction volume. Fuel concentration within this "packet" will be monotonically decreasing due to diffusion, dilution, and reaction. Oxygen concentration will first rise from diffusion and turbulent mixing, reaching a maximum when complete mixing has occurred. Thus of concern (and truly the one that could prove fatal in the case of Phosphonofluoridic acid esters) is the time-temperature history of the compound. A distribution of paths (mechanical as well as chemical) exist. Some of these paths may have elemental volumes where little or no mixing has taken place, or where the temperature is 200-300° below the mean gas temperature. A very small percentage of material passing along such a path can drastically change the destruction efficiency of a unit. For example, if a unit can achieve greater than ten nines destruction for 99% of the gas, but less than one nine for 1%, the overall efficiency will be less than three nines!

DEAN WOLBACH
Senior Scientist,
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Acurex Corp.
Mountain View, CA.

On "Waste Incineration and Heat Recovery"

To the editor:

I enjoyed the recent article that reviewed environmental considerations on waste incineration [Ward, J. and Ting, A., *Environmental Progress*, 1, 30 (1982)]. However, I believe that the section entitled "Nitro Groups" may be somewhat incomplete. In particular, I'm referring to the comments regarding the fractional conversion of the bound nitrogen compound to NO_x versus bound nitrogen compound concentration in the fuel. Figure 6 of the text contains an inverse relationship for 100% theoretical air. The studies cited (references 15 and 16 of article) contain excellent information concerning NO_x formation when combusting fuels containing a multitude of different bound nitrogen species. However, another study (Appleton, J. and Heywood, J., "The Effects of Imperfect Fuel-Air Mixing in a Burner on NO Formation from Nitrogen in the Air and the Fuel", 14th International Combustion Institute Meeting, Penn State, August, 1962, 777-786) gives different results for the combustion of fuels containing bound nitrogen compounds. Figure 8 of this study shows that the percent conversion of the bound nitrogen compound to NO_x is a strong function of the premixed state of the mixture and not the percent bound nitrogen compound. For instance, they used 0.5 weight % pyridine and obtained from 50% to 100% conversion to NO_x depending on the nozzle atomizing air pressure (a variable affecting the degree of premixing).

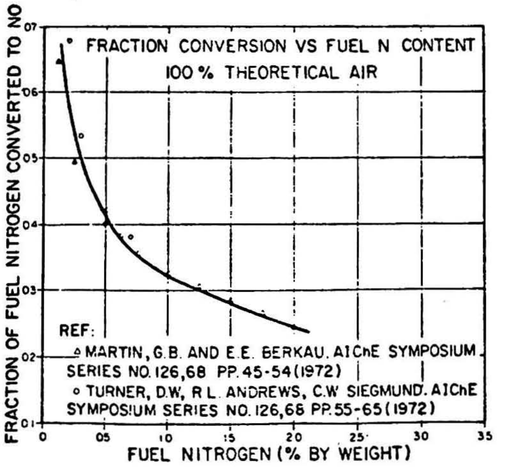

Fig. 6. Fraction conversion vs. fuel N content. 100% theoretical air Ward, J. and Ting, A., "Waste Incineration and Heat Recovery", [*Environmental Progress*, 1, 30 (1982)].

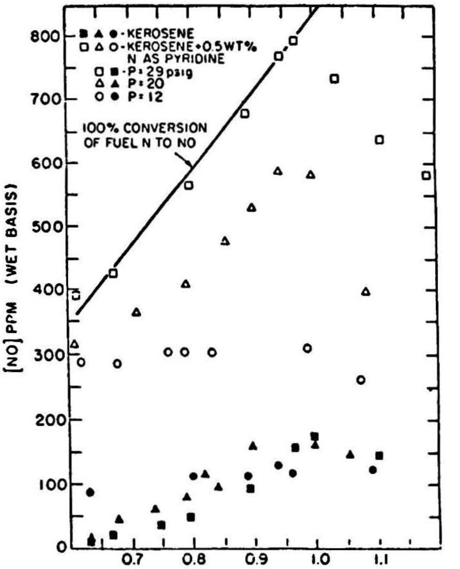

Fig. 8. Measured burner-exhaust NO concentrations for pure kerosene (solid points) and kerosene with 0.5 per cent by weight of pyridine for different atomizing air pressures. Solid line shows 100 per cent conversion of nitrogen in the pyridine. [Appleton, J. and Heywood, J., "The Effects of Imperfect Fuel-Air Mixing in a Burner on NO Formation from Nitrogen in the Air and the Fuel", 14th International Combustion Institute Meeting, Penn State, August, (1982), 777-786].

Using Figure 6 of the Ward and Ting article, the 0.5% pyridine should have resulted in only 40% conversion to NO_x. Basically, this means that in studying combustion of fuels with bound nitrogen in excess air, it is the degree of mixing that is the important variable not the fuel bound nitrogen content. The studies with a poor fuel atomization actually represent a staged combustion (fuel rich followed by fuel lean), while the studies with good fuel atomization approach a premixed, prevaporized combustor.

It has been about five years since I have done research in this area but the Appleton and Heywood article aided greatly in the interpretation of combustion data using bound nitrogen compounds in rich and lean operation as well as multi-stage combustion. For this reason I think it should be included in any review on NO_x formation involving bound nitrogen species.

Ronald M. Heck
Research and Development Dept.
Engelhard Industries Division
Edison, NJ.

On "Soluble-Sulfide Precipitation for Heavy Metals Removal from Wastewaters"

To the editor:

Without knowing all of the circumstances concerning the pilot plant operation, truly apropos comment is difficult, but I would like to make three general observations on this article [*Environmental Progress*, 2, 110 (1982)].

First, the solubility products of the sulfides of the six metals listed vary from Cu^+ at 2×10^{-47} to Zn^{++} at 1.2×10^{-23} (except no figure was available for any chromium sulfide.) I have had some limited experience in using both BaS and $Na_2S \cdot 9H_2O$, with mixtures of sulfates of several metals and found that the metal with the smallest solubility produce invariably precipitated almost completely before the metal with the next larger solubility product started to precipitate. Hence, I was surprised to see any copper or cadmium (3.6×10^{-29}) nickel (1.4×10^{-24}) of zinc had occurred. There are undoubtedly good explanations but the table results caught my attention.

Secondly sulfides are fairly readily oxidized by chemical or bacteriological action to sulfates, which are generally rather soluble, therefore, even if immediate leaching tests show low discharges, the results in a few years may be very different.

My third point is to wonder why BaS was not tried or at least discussed. In many areas of the country, too much sodium is already in streams. Barium is, of course, an undesirable heavy metal in streams but if any sulfate ions are present or could be introduced, $BaSO_4$ is quite insoluble and could be precipitated prior to discharge to a stream. Finally, at least a few years ago, the sulfide ion of barium was considerably less expensive than the ion of sodium.

E. B. Pugsley
4505 S. Yosemite St. #415
Denver, CO

Engineering Control of Odors

Every industrial odor-control problem must be regarded individually as an engineering exercise in applied research.

Richard A. Duffee, TRC-Environmental Consultants, Inc., Wethersfield, Conn. 06109

Odor control may be the most challenging area to the environmental pollution-control engineer. There are several reasons for this. Most significant, perhaps, is the lack of any—not merely uniform—standards as to what constitutes an acceptable odor. As a result, each odor-control problem becomes—or should—an exercise in applied research to determine what sources of odorous emissions to control and to what extent to eliminate community odor complaints. One can neglect this only at the risk of greatly exacerbating the problem, as well as wasting considerable amounts of time and money.

The second underlying reason for the challenge of odor control is the extremely small amount of odorant that triggers odor perception in humans. Some odorants can be detected in vapor concentrations as low as 0.001 parts per billion. As a result of our olfactory acuity, ordinarily minor sources for most pollutants—e.g., evaporation from waste-treatment ponds or impoundments, spills, leaks from valves and flanges, vents from tanks or filling operations—may be the primary source. Also, the concentration of odorants in typical emission sources is usually in the parts-per-million (ppm) range. To minimize or to eliminate odor detection frequently requires reducing odorant concentrations to the parts-per-billion (ppb) range, i.e., overall control efficiencies upwards of 99 percent.

The final basis for the challenge of odor control is that one is dealing with an effect, i.e., our conscious reaction to a stimulus of our olfactory system by odorants in the gaseous or vapor state. While one can quantify several odor properties such as intensity or detectability, as well as odorant concentration, one has only a limited understanding of the relation of these measures to the resulting level of annoyance. (Remember, the objective of odor control is to eliminate objectionable odors not all odor). Ability to detect odor increases in parts of the populace with increased frequency of exposure to certain odorants with an associated increase in their level of annoyance. Consequently, designing to so-called threshold concentrations frequently will not eliminate odor complaints where the population is sensitized.

Because one is dealing with an effect, odor control can be directed either at reducing the concentration of odorants at the receptor (the human nose) or at interfering with the receptor's olfaction process [*1*]. Approaches to odor control aimed at reducing odorant concentration at the receptor are:

- Process modification
- Atmospheric dispersion
- Absorption and gas-phase reactions
- Adsorption
- High-temperature oxidation

The techniques that interfere with the olfaction process are commonly grouped under the term "odor modification." These include:

- Counteraction—denotes reduction in intensity of the malodorant
- Cancellation—means reduction to zero intensity never convincingly documented
- Masking—refers to a change in odor quality that makes the malodorant unrecognizable; implies concealment

These will not be discussed, since they do not represent engineering controls of odor.

In the following sections, each of the odorant control techniques is reviewed briefly with respect to principles of design and operation. Comparative costs are also included as a guide to method selection.

For a fuller discussion of these topics the reader is referred to the section on odor control in the report by the National Research Council Committee on Odors From Stationary and Mobile Sources, published by the National Academy of Sciences in 1979 [2].

PROCESS MODIFICATION

The simplest way to solve odor problems is to prevent them—not by applying sophisticated and costly technology but merely by being aware of potential odor problems. For example, many odor problems can be eliminated simply by using less odorous materials, e.g., substitute glycols or refined mineral oil for aromatic solvents. Odorous emissions can be reduced substantially by operating drying systems at lower temperatures. Chilling the water in condensers can increase their effectiveness. Conversely, raising the temperature in combustion equipment used for waste treatment can prevent formation of partially oxidized intermediates more odorous than the original waste.

Pressure should also be carefully considered. Simply maintaining a slight negative pressure in process equipment or in production facilities minimizes fugitive emissions and makes the odor-control job easier.

Volume is one of the most important considerations. A large dilution ventilation volume may be desirable to maintain worker comfort and safety. However, this can increase the discharge of volatile odorants to the atmosphere and negate the efficiency of certain odor-control alternatives such as scrubbers. Careful exhausting of process emissions, including such things as drain junction boxes and sewer vents, can greatly reduce ventilation volumes. The resulting energy savings, in fact, can offset the cost of the odor-control system.

Two of the major contributors to odor problems are poor maintenance and poor housekeeping. In many odorous processes, the greatest amount of odorant released is from leaks (from flanges, pumps, seals, open vessels, etc.). Continued maintenance can prevent this type of problem. Sim-

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ilarly, processes involving odor-producing materials such as putrescible foods or food by-products or volatile materials must be kept scrupulously clean to prevent odor problems.

ATMOSPHERIC DISPERSION AND LAND-USE PLANNING

Many odor problems result from exhausting odorous emissions through ventilating fans or through stub vents or ducts on the roof in such a manner that they are immediately entrained in the building wake and become, in effect, ground-level sources. Solving these problems frequently involves discharging these exhausts through a stack tall enough to prevent capture of the odorous exhaust in the building wake. But beware—this does not necessarily mean a good-engineering-practice (GEP) stack height of 2½ times the height of the building roof, which is frequently woefully inadequate. The requisite stack height can only be determined by either 1) a puff dispersion model that incorporates building-wake effects; 2) a physical model/wind tunnel simulation; or 3) tracer experiments on the actual facility.

Odor control by atmospheric dispersion is predicated on the assumption that dilution of odorants to below a sensory target value—e.g., the detection threshold—can be achieved and maintaind by atmospheric dispersion. This assumption relies heavily both on the validity of reported odorant thresholds and on the accuracy of measurements of odorous emission. Published odorant thresholds are more a function of the measurement method used than an absolute indicator. The same observation may be made with respect to measurement of odorant emission rates; in this case, however, with careful selection of method and adaptation to the source, accurate and reliable measurement can be made.

Since there are no federal EPA odor regulations, neither is there an EPA ban on using atmospheric dispersion for odor control. Atmospheric dilution of odorous emission can be achieved in two main ways:

- Collection of all process and plant emission and discharge through a tall stack: Contaminants emitted into the atmosphere are diluted by turbulence and diffusion. The dilution of a contaminant depends directly on the wind speed: the mass emitted in unit time is spread over the distance traveled in unit time by air blowing over the discharge point. In addition to this thinning of material in the direction of the mean wind, there is mixing along and across the mean wind horizontally and vertical mixing because of the natural turbulence resulting from the wind.
- Relocation of the source at a greater distance from any receptor: Moving an odorous discharge farther from any receptor obviously results in a reduced odorant concentration at the receptor. Such a drastic step is currently limited to situations where the source may be relocated within the confines of property to take advantage of favorable atmospheric dispersion provided by local climate and topography. These situations arise most often during siting studies. Careful assessment by use of physical or dispersion models of industrial-plant odor sources before the location of a plant is fixed can avoid odor problems.

Several factors must be carefully considered before reliance is placed on atmospheric dispersion for odor control. These include the characteristics of the odorants and their sources and local meteorologic characteristics. Point sources—such as ducts, ports, and vents—are suitable for dispersion. Fugitive emission—such as that from open doors, windows, or leaking flanges—should be prevented or captured and ducted to the stack. Terrain must also be considered. If the odor source is in a valley in rugged, complex terrain, odor control by dispersion is either impractical or impossible; in such cases, discharging odorants through a tall stack only transfers the location of complaints of malodors. The following steps should be followed when discharge through a tall stack is selected as the means of controlling odors:

- Measure the odor emission per source. Dilution ratio and standard flow rate are measured at each potentially odorous emission source.
- Perform modeling calculations from the present or design source configuration with a puff model, such as the TRC Odor Model [3] which includes plume rise, building-wake entrainment, and mixing-volume correction techniques designed to increase accuracy.
- Conduct an odor survey in the community. This involves the mapping of perceived odor qualities (or characteristic smell) and odor dilution ratios and/or intensities under different meteorologic conditions, usually on the basis of tests with expert odor judges.
- Correlate the model results with the survey results (i.e., calibrate the model). This will relate the odor intensities, dilution ratios, and types found in the community with those determined by modeling suspected sources. If there is no correlation, this could mean that the odor source configuration is more complex than anticipated or that a significant contribution to the odor problem has been neglected or incorrectly represented in the model. The model should be adjusted accordingly.
- Determine required stack height. The adjusted model should be used for the determination of the stack height required to reduce the odor impact at receptors to less than the selected target value.

ABSORPTION AND GAS-PHASE REACTIONS

Scrubbing of odorous emissions is a widely used means of odor control. Non-chemical absorption, i.e., involving only solution of the odorants in an appropriate solvent (usually water) is widely used for removal of soluble inorganic gases such as HCl and NH_3. Most odorants, however, are organic compounds with limited solubility in water. Accordingly, most odorant scrubbing applications involve use of solvents which not only dissolve the odorants—a fundamental requirement for scrubbing—but also react with the odorants to prevent their revolatization from the scrubbing liquid. Since most odorous emissions involve mixtures of numerous odorants, multiple—stage scrubbing is becoming more common, using different scrubbing liquors in each stage. Frequently, injection of an oxidant (usually Cl_2) into the odorous exhaust upstream of the scrubber is used to react with the odorants in the gas phase to make them either less odorous or more soluble or both. Since these oxidants are soluble in the scrubbing liquid, they become powerful oxidants for the absorbed odorants.

For applications involving very low odorant concentrations and requiring maximum mass-transfer rates, countercurrent packed towers are used. Maximum odor-control efficiencies for single-stage towers are approximately 95 percent because of mass-transfer limitations. For somewhat higher concentrations or multistage scrubber operations, cross-flow packed beds are most often used with dilute, recycled sulfuric acid and dilute, recycled caustic as the primary scrubbing liquids. Such systems can achieve odor control efficiencies of 97 percent or better. Other commonly used scrubbing liquors are sodium hypochlorite for aldehydes, organic acids, amines and sulfides, sodium or calcium bisulfite for aldehyde control, and mineral oil or glycol for miscellaneous volatile organics [*4*].

Careful design is needed for scrubbing applications to prevent plugging of the packing by particulate matter, to maintain adequate liquid/gas ratios usually in the range of 5-10 gpm (19-38 L/min)/(28.3 m^3/min)), and to control chemical feed rates. For example, careful control of chemical feed is vital when using Cl_2 or hypochlorite to prevent discharging strong chlorine-like odors.

ADSORPTION

Any gas or vapor will adhere to some degree to any solid surface. This phenomenon is called "adsorption." Practical adsorbents have extensive areas of inner surface, by reason of extensive honeycombing. When adsorbed matter condenses in the submicroscopic pores of an adsorbent, the phenomenon is called "capillary condensation." Adsorption is useful in odor control, because it is a means of concentrating gaseous odorants from an airstream, thus facilitating their disposal, their recovery, or their conversion to innocuous or valuable products. When an odorous airstream is passed through a fresh adsorbent bed, almost all the odorant molecules that reach the surface are adsorbed, and desorption is very slow. Furthermore, if the bed consists of closely packed granules, the distance the molecules must travel to reach some point on the surface is small, and the transfer rate is therefore high. In practice, the half-life of airborne molecules streaming through a packed adsorbent bed is around 0.01 s, and a 95% removal occurs in about 4 half-lives, or around 0.04 s [5]. Thus, the very high efficiencies required to deodorize a highly odorous airstream may be achieved with a bed of moderate depth at reasonable airflow rates.

The quantity of material that can be adsorbed by a given weight of adsorbent depends on the following factors: the concentration of the material in the space around the adsorbent, the total surface area of the adsorbent, the total volume of pores in the adsorbent with diameters small enough to facilitate condensation of adsorbed gases, the temperature, the presence of other gases in the environment that may compete for a place on the adsorbent, the characteristics of the molecules to be adsorbed (especially their weight, electric polarity, size, and shape), and the electric polarity of the adsorbent surface. Maximal capacity for adsorption of a given substance is favored by a high concentration of the substance in the space adjoining the adsorbent, a large adsorbing surface, freedom from competing substances, low temperature, and aggregation of the substance in large molecules that fit and are strongly attracted to the receiving shapes of the adsorbent [6].

Adsorbed odorants may be disposed of in any of the following ways: the adsorbent with its adsorbate may be discarded; the adsorbate may be desorbed and recovered, if it is valuable, or discarded (the adsorbent is recovered in either case), or the adsorbate may be chemically converted to a more easily disposed product.

There are basically two adsorbents widely used for industrial odor control, activated carbon, often impregnated for specialized applications, and activated alumina impregnated with potassium permanganate (which has the tradename of Purafil). Activated carbon will adsorb most organic odorants, especially non-polar. For typical industrial applications, thick-bed adsorbers are used with onsite regeneration of the carbon by superheated stream. This system involves two carbon beds. One carbon bed is adsorbing while the other is being regenerated. Bed depths are in the range of 1 to 6 feet (0.3-1.83 m) and air flow capacities up to 40,000 cfm. (1,132 m^3/min). The carbon in this system can last for years with odor-control efficiencies in excess of 95 percent. The period between regeneration is usually in the range of 2 to 10 hours, but this is highly variable and must be determined for each application.

Thin-bed adsorbers are used for light odorant loads (ppb to low ppm range) and consist of carbon beds of approximately 1-in (0.25 m) depth in flat, cylindrical, or pleated shapes. Single cells handle 750-1000 cfm (21.2-28.3 m^3/min), while aggregates of flat-bed components handle 2000 cfm (56.6 m^3/min). Thin-bed adsorbers are expected to have service lives of several months. They are usually replaced when exhausted.

Impregnated activated alumina is used in similar configurations as thin-bed carbon adsorbers. It is used primarily to control easily oxidizable odorants including formaldehyde and hydrogen sulfide. Typical applications of impregnated adsorbents are shown in Table 1 [8].

HIGH TEMPERATURE OXIDATION [7]

High-temperature oxidation is an air-pollution control process in which odorous waste oganic gases or organic particles are converted to odorless gaseous products, such as carbon dioxide and water vapor. The odors are destroyed by exposure of the waste gases to the proper conditions of temperature, time, and turbulence in the presence of air in a combustion chamber. The temperature required depends on the specific contaminants involved and the design configuration of the equipment used. This method will completely destroy the odors in the waste gases at some temperature if the control equipment has been properly designed.

Oxidation temperatures range mainly from about 600 to 1,500°F (about 315 to 815°C). Residence times can range

TABLE 1. ADSORBENT IMPREGNATIONS[a]

Adsorbent	Impregnant	Pollutant	Action
Activated carbon	Bromine	Ethylene; other alkenes	Conversion to dibromide, which remains on carbon
	Lead acetate	H_2S	Conversion to PbS
	Phosphoric acid	NH_3; amines	Neutralization
	Sodium silicate	HF	Conversion to fluorosilicates
	Iodine	Mercury	Conversion to HgI_2
	Sulfur	Mercury	Conversion to HgS
	Sodium sulfite	Formaldehyde	Conversion to addition product
	Sodium carbonate or bicarbonate	Acidic vapors	Neutralization
	Oxides of Cu, Cr, V, etc.; noble metals (Pd, Pt)	Oxidizable gases, including reduced sulfur compounds such as H_2S, COS, and mercaptans	Catalysis of air oxidation
Activated alumina	Potassium permanganate	Easily oxidizable gases, especially formaldehyde	Oxidation
	Sodium carbonate or bicarbonate	Acidic gases	Neutralization

[a] Reprinted with permission from Turk.

from less than a second to about 2 s. Turbulence (on the basis of a calculated average velocity at the outlet from the combustion chamber) can be as high as about 30 ft/s (9.1 m/s) at oxidation temperature.

Some odorous inorganic combustibles—such as hydrogen sulfide, ammonia, and cyanides—can be destroyed by high-temperature oxidation, but there is a limit on the concentration of inorganic combustibles in the waste gas stream that can be satisfactorily controlled, because these substances are converted by oxidation to their oxides, which can be objectionable themselves at high concentrations.

Odor problems that ordinarily cannot be satisfactorily controlled by high-temperature oxidation alone are those in which the waste gases contain halogen compounds or compounds (such as phosphates) that form objectionable oxides or acids. When odorous waste gases containing halogens are oxidized, the reaction products include free halogens (fluorine, chlorine, bromine, or iodine), halogen acids, phosgene, etc., all of which are toxic or corrosive and must be removed by chemical scrubbing before discharge to the atmosphere. In the case of phosphates, the treated gases contain phosphorus oxides or acids, which are toxic and also have to be removed.

Several methods of high-temperature oxidation are applicable to controlling odorous waste gases in which contaminants are present in concentrations below the LEL: direct-flame oxidation, catalytic oxidation, and use as the combustion air supply for any plant combustion equipment, such as boilers and air heaters. The maximal concentration of odorous waste gases processed in high-temperature oxidation equipment is usually limited, by insurance underwriters, to 25% of the LEL, to eliminate fire hazards. This limitation ensures that the vapor-air mixture being oxidized will not ignite when exposed to a spark or flame. In some cases with continuous monitoring equipment, concentrations as high as 40 or 50% of the LEL are permitted. In most instances of odor nuisance, the concentration of the contaminating vapors is well below 25% of the LEL—and in many cases, as low as a few parts per million by volume.

In direct-flame oxidation, the odorous emission in concentrations well below the LEL is completely oxidized to nonodorous gases, such as carbon dioxide and water vapor, by exposure to temperatures of 900-1600°F (480-815°C) in the presence of a flame. The temperature required to do an effective job depends on the specific pollutants involved and the design of the combustion chamber. It has been shown that temperatures of 900-1600°F (480-815°C), velocities of 15-30 ft/s (4.6-9.1 m/s), and residence times (including flame contact time) of 0.25-0.60 s give satisfactory cleanup.

In catalytic oxidation, the presence of a catalyst allows high-temperature oxidation to take place at a lower temperature and in the absence of a flame. However, a burner is usually required to heat the odorous waste gases to the required temperatures, and the gases are partially oxidized before they reach the catalyst. In catalyst systems, the type of catalyst, the oxidation temperature, the velocity through the bed, and the amount of catalyst are important variables that affect efficiency. Platinum and mixed noble-metal catalysts have been used predominantly in catalytic oxidation equipment for the control of industrial air pollutants. The catalyst does not participate in the reaction. Although the precise mechanism of heterogeneous catalytic oxidaton is not well understood, there is general agreement that it proceeds through three necessary steps (and in this order): adsorption on the active surface, chemical reaction (oxidation on surface), and desorption of the reaction products.

The oxidation temperature for a catalyst system is the average temperature of the gases leaving the catalyst bed and ranges from about 600°F to 1200°F (about 315°C to 650°C). There is a temperature rise across the bed that depends on the amount of the contaminant that is oxidized.

The major problems with catalyst systems are the difficulty in obtaining uniform flow and uniform temperature distribution and the susceptibility of catalysts to deterioration due to poisoning, suppression, and fouling (Table 2), or due to attrition. Another concern is that catalytic condition is difficult to monitor, compared with the ease of monitoring temperature only in a direct-flame oxidation system. Any high-temperature oxidation system that operates inefficiently for any reason will yield intermediate oxidation products, such as pungent aldehydes and acrylates and burnt odors. With direct-flame oxidation, once the temperature for proper oxidation has been determined in a field test, maintenance of that temperature should ensure proper operation of the system. That is not true for a catalyst system, because higher operating temperatures are required as the catalyst deteriorates.

COSTS

The costs of odor-control systems vary with application and depend on a number of factors, such as volume of gas, size of equipment, odorant composition and concentration, and degree of control required. Consequently, the comparative costs of the various control techniques presented in Table 3 are to be taken only as broad guidelines not definitive estimates.

Operating costs are highly variable and are very much site specific. Scrubbers handling 20,000 cfm (566 m^3/min) will have energy costs for fans, etc., of approximately $4,000 per year based on a rate of $0.015 per kWh. A stack 100 ft (30.5 m) in height will have similar energy operating costs.

Chemical costs for a two-stage scrubber using dilute sulfuric and dilute caustic with chlorine injection upstream would be approximately equal to another $4,000 per year for a 20,000-cfm (566 m^3/min) system.

Operating costs for carbon systems are highly variable as shown in Table 4.

Annualized costs for catalytic oxidizers are shown in Table 5. For low pollutant concentrations of 100 ppm or less, operating costs for a 20,000-cfm (566 m^3/min) direct-flame system with heat recovery is approximately $180,000/yr. This means that controlling odor sources by high-temperature oxidation can become prohibitively expensive.

In summation, the most cost-effective way to solve odor problems is to prevent them by proper siting and process design, and by good maintenance and housekeeping practices. Atmospheric dispersion may be used as a means of odor control, especially to prevent entrainment of exhaust in building wake. When required stack height exceeds approximately 150 ft (45.7 m), other control methods become comparably cost-effective.

In choosing between absorption (scrubbing), adsorption or thermal oxidation, consideration must be given to degree of control required, type and concentration of odor-

TABLE 2. [7] TYPICAL POISONS, SUPPRESSANTS, AND FOULING AGENTS THAT AFFECT CATALYSTS OF THE PLATINUM-METALS

Type of Agent	
Poison	Heavy metals Phosphates Arsenic
Suppressant	Halogens (both as elements and in compounds) Sulfur compounds
Fouling Agent	Inorganic particles Alumina and silica dust Iron oxides Silicones

TABLE 3. COMPARATIVE CAPITAL COSTS OF ENGINEERING ODOR CONTROL METHODS

Method	Type of System	Approximate Capital Cost
Stack Dispersion	50-foot (17.24-m) guyed stack	$ 7,000
	Small diameter	
	100-foot (30.48-m) guyed stack	$13,000
	200-foot (60.96-m) self-supporting	$250,000
	300-foot (91.44-m) self-supporting	$400,000
Absorption	FRP scrubber only	$1.3-3.0/cfm ($46-106/m³/min)
	fans, pumps, piping, etc.	$2.5-3.5/cfm ($88-124/m³/min)
Adsorption	Dual-bed regenerable	$10-15/cfm ($353-530/m³/min)
	Thin-bed adsorber	$4-7/cfm ($141-247/m³/min)
High-Temperature Oxidation	Direct Flame—with heat recovery	$10-25/cfm ($353-883/m³/min)
	Catalytic—with heat recovery	$10-30/cfm ($353-1059)/m³/min)

TABLE 4. [6] COMPONENTS OF ANNUALIZED COSTS (SAVINGS) FOR ADSORPTION AND ADSORPTION-INCINERATION SYSTEMS[a]

Configuration:	1. Dual fixed-bed absorber operating at 100°F (38°C) 2. Solvent recovery with condenser and decanter	1. Dual fixed-bed adsorber operating at 100°F(38°C) 2. Thermal incineration with primary heat recovery
Gas-stream characteristics:		
Flow	20,000 scfm (566 m³/min)	20,000 scfm (566 m³/min)
Concentration	25% LEL	25% LEL
Process-gas temperature	170°F (77°C)	375°F (191° C)
Direct operating costs:		
Utilities	$48,700[b]	70,200[b]
Direct labor	3,000[c]	3,000[c]
Maintenance	15,400[d]	18,400[d]
Carbon replacement	11,500[e]	11,500[e]
Capital charges:	80,850[f]	96,500[f]
Recovery (credits):	(333,400)[g]	—
Total net annualized costs (credits):	(173,950)[h]	199,600

[a] Derived from Radian Corporation.
[b] Cooling water at $0.045/1,000 gal ($0.011/1000 L); steam at $2/1,000 lb ($4.40/1,000 kg); electricity at ?
[c] Labor at $8.25/h.
[d] Maintenance as 4% of the capital cost.
[e] Carbon at $0.72/lb ($1.58/kg), with 20% of carbon replenished each year.
[f] Capital charges included as percent of capital cost: depreciation, 12%; taxes, insurance, and overhead, 4%; interest, 5%.
[g] Benzene credited at $0.90/gal ($0.24/L), hexane at $0.50/gal ($0.13/L).
[h] Net costs calculated as capital charges + direct operating costs — recovery credits.

TABLE 5 [7]. TYPICAL COMPONENTS OF ANNUALIZED COSTS OF CATALYTIC AFTERBURNERS[a]

Gas-stream characteristics:	
Flow	15,000 scfm (7 m³/s)
Concentration	15% LEL
Inlet temperature	300°F (150°C)
Direct operating costs:	
Utilities	$20,000[b]
Direct labor	3,000[c]
Maintenance	7,800[d]
Annualized catalyst replacement	19,800[e]
Capital charges:	41,000[f]
Total:	$91,600

[a] Reprinted with permisson from Hirt Combustion Engineers.
[b] Fuel at $1.56/GJ ($1.65/10⁶ Btu), electricity at $9.17/GJ ($0.033/kWh).
[c] Labor at $8.25/man-hour.
[d] Maintenance as percentage of capital cost: 4%.
[e] Catalyst life of 3 yrs.
[f] Capital charges include as percentages of capital cost: depreciation, 13%; and taxes, insurance, and administrative overhead, 4%.

ants. In all cases, the volume of air to be treated should be minimized. Scrubbing will usually involve lower capital costs than either adsorption or thermal oxidation, but may require higher operating or maintenance costs.

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Diethylenetriamine Solutions for Stack Gas Desulfurization by Absorption/Stripping

Drastic reductions in steam consumption can be realized in a simple absorption/stripping process.

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Absorption/stripping is a potentially attractive method of desulfurizing stack gas with the production of concentrated SO_2 [1,2]. SO_2 is absorbed from stack gas containing 500 to 5000 ppm SO_2 by an aqueous solution at 30 to 60°C. The solution is regenerated by stripping with steam at 80 to 120°C. Water is easily condensed from the stripper overhead vapor, leaving concentrated SO_2. This process has not received commercial acceptance because of excessive steam requirements.

This paper reports on work which is a part of a development program on absorption/stripping sponsored by the Electric Power Research Institute [3]. Previous portions of the program concentrated on the use of sodium citrate solution [3,4,5], and screened the use of glyoxylic acid, basic aluminum salts, and ethylenediamine [6].

Diethylenetriamine (DETA) was first proposed as an aqueous absorbent for SO_2 by Roberson and Marks [7]. Johnstone *et al.* [2] recognized that weak bases with buffer capacity between pH 4 and 6 should minimize steam requirements for absorption/stripping because their pH values decrease with increasing temperature. DETA gives solutions with such properties, is nonvolatile at absorber conditions, and is commercially available at about $2.70 /kg [8].

This paper characterizes DETA solutions by experimental data and correlations of pH behavior [9], SO_2 vapor pressure, and absorbent stability at absorber and stripper conditions [10]. These data have been used to estimate steam requirements of a simple absorption/stripping process.

pH BEHAVIOR

Previous pH measurements found DETA dissociation constants and heats of neutralization at 10 to 40°C in dilute solutions [11, 12]. This work measured values of pk_l and ΔH_l for DETA and pk for sulfite/bisulfite at 25 to 96°C in 0.00667 to 1.6 m DETA neutralized by HCl, H_2SO_4, and/or SO_2.

At pH values typical of absorption/stripping, DETA buffers by the reaction:

$$DETAH_2^{+2} + H^+ \rightleftarrows DETAH_3^{+3}$$

$$pK_1 = -\log\left(\frac{a_{H^+}a_{DETAH2^{+2}}}{a_{DETAH_3^{+3}}}\right)$$

At 25°C and infinite dilution, pK_1 is 3.64 and ΔH_1 is −7.6 kcal/gmol [11]. Other reported values of ΔH_1 are −7.3 kcal/gmol [13] and −8.2 kcal/gmol [12].

With high concentrations of dissolved SO_2 the sulfite/bisulfite buffer can also be important [14]:

$$SO_3^{=} + H^+ \rightleftarrows HSO_3^-$$

$$pK_s = -\log\left(\frac{a_{H^+}a_{SO_3^=}}{a_{HSO_3^-}}\right) = 6.91$$

$$\Delta H_s = -0.89 \text{ kcal/gmol}$$

In concentrated solutions the effective dissociation constants are defined by:

$$pk_l = -\log\left(a_{H^+}\frac{[DETAH_2^{+2}]}{[DETAH_3^{+3}]}\right) \qquad (1)$$

$$pk_s' = -\log\left(a_{H^+}\frac{[SO_3^=]}{[HSO_3^-]}\right) \qquad (2)$$

Because the effects on activity coefficients of ionic strength and ion interactions are greater for more highly charged ions, pk_l will increase and pk_s will decrease in more concentrated solutions. At 1.3 m ionic strength, Jonassen *et al.* [12] reported pk_l of 4.78.

Because DETA is a weak base, pk_l decreases with increasing temperature:

$$\frac{dpk_l}{d(1/T)} = \frac{-\Delta H_l}{2.303R} \qquad (3)$$

In the absence of other buffers, solution pH is directly related to pk_l and pH decreases with increasing temperature:

$$\frac{dpH}{d(1/T)} = \frac{-\Delta H_l}{2.303R} \qquad (4)$$

In DETA solutions with high concentrations of dissolved SO_2, buffering by sulfite/bisulfite will tend to reduce the increase of pH with temperature because ΔH_s is positive.

The desired operating pH for absorption/stripping can be obtained by neutralizing aqueous solutions of DETA with SO_2 and either sulfuric or hydrochloric acid. Assuming that dissolved SO_2 appears as bisulfite, the fraction neutralization is given by:

$$f = \frac{C_{SO_2} + C_{Cl} + C_{SO_4} - C_{Na}}{3C_D} \qquad (5)$$

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In solutions containing SO_2 and DETA, pH can be obtained in terms of k_1 and k_s from the relationship:

$$\begin{aligned} a_H^3 + & + [3C_D - C_{SO_2} - 2C_{SO_4} - C_{Cl} + k_1 + k_s]a_H^2 + \\ & + [(3k_s + 2k_1)C_D - (2k_s + k_1)C_{SO_2} - (k_1 + k_s)C_{Cl} \\ & - 2(k_1 + k_s)C_{SO_4} + k_1k_s]a_H + \\ & + k_1k_s(2C_D - 2C_{SO_2} - C_{Cl} - 2C_{SO_4}) = 0 \end{aligned} \tag{6}$$

This model neglects concentrations of undissociated SO_2, $DETAH^+$, and DETA species and is limited to a pH range of 4.0 to 6.0.

Experimental Procedures

DETA buffer solutions were prepared from reagent grade DETA, HCl, and H_2SO_4. Dissolved SO_2 was obtained by sparging with pure SO_2 or by adding $NaHSO_3$ solids. The actual SO_2 concentration was determined by iodimetric titration. 0.1 wt. % hydroquinone was added to inhibit oxidation. Compositions are reported as molarity (m̲ = gmol/liter) or molality (m = gmol/kg H_2O).

Measurements of pH were made with combination electrodes calibrated by pH 4.00 and pH 7.00 buffers. At 25°C, measurements were made with a Ag/AgCl electrode. Measurements at 55 and 95°C, were made with a Thalamid electrode, which was conditioned in a pH 4.00 buffer by holding it at 55 or 95°C for at least 24 hours.

Effects of Ionic Environment and Temperature

Table 1 gives pk_1 values and heats of neutralization measured at 26 to 96°C in solutions with 83.3% neutralization of the DETA. The pk_1 values were taken to be equal to the measured pH.

The pk_1 values increased with apparent ionic strength and were greatest in solutions of Na_2SO_4, probably because more $SO_4^=$ is available for ion pairing with the DETA species. At ambient temperature with an ionic strength of 1.5, the pk_1 value was 5.91 in Na_2SO_4 solution and 4.78 in DETA/HCl solution. This compares to 3.64 at infinite dilution. The presence of $NaHSO_3$ significantly reduces the apparent pk_1, because the $SO_3^= / HSO_3^-$ buffer was neglected in assuming pk_1 equal to pH at 83.3% neutralization.

The heat of neutralization was estimated using pairs of pH data at different temperatures. In the absence of dissolved SO_2, ΔH_1 was about -8.4 kcal/gmol in solution neutralized by HCl and -7.0 kcal/gmol in solutions neutralized by H_2SO_4. In solutions neutralized by H_2SO_4 and SO_2, the heat of neutralization was as low as -4.0 kcal/gmol, because of the influence of the sulfite/bisulfite buffer.

Effects of Solution Composition

Extensive pH measurements were made at 25°C in solutions containing 0.4, 0.8, and 1.6 m DETA with variable levels of H_2SO_4, HCl, and SO_2. Each series of measure-

TABLE 1: APPARENT pk_1^a VALUES OF DETA

Composition (m̲)	Ionic Strength (equiv/liter)	T (°C)	Apparent pk_1^a	Heat of Neutralization (kcal/gmol)
Ideal [11]	0.0	25	3.64	-7.6
0.00667 DETA				
0.01667 HCl				
0.3 NaCl	0.3	27	4.72	
1.5 NaCl	1.5	27	4.99	
0.1 $CaCl_2$	0.3	27	4.62	
0.1 Na_2SO_4	0.3	27	5.48	
0.5 Na_2SO_4	1.5	26	5.91	
0.0522 DETA	0.3	26	4.98	-6.9
0.0652 H_2SO_4		95	4.03	
		27	4.93	
0.261 DETA	1.5	26	5.40	-7.6
0.326 H_2SO_4		96	4.36	
1.00 DETA	5.75	27	5.73	-6.5
1.25 H_2SO_4		94	4.87	
0.333 DETA	1.5	26	4.78	-8.2
0.833 HCl		94	3.67	
0.0667 DETA	0.3	26	4.49	-8.6
0.167 HCl		95	3.32	
0.222 DETA	1.5	26	5.18	-6.1
0.222 $NaHSO_2$		96	4.34	
0.278 H_2SO_4				
1.00 DETA	6.75	27	5.33	-4.0
1.00 $NaHSO_3$		60	5.11	
1.25 H_2SO_4		27	5.28	
		27	5.28	
		94	4.85	

[a] Apparent pk_1 = pH when DETA is 83.3% neutralized by acid.

ments was correlated using Equation 6 to give values of pk_1 and pk_s. Table 2 gives a summary of the measured values of pk_1 and pk_s in solutions with HCl and H_2SO_4.

Empirically, the effects of DETA concentration and acid to DETA ratio are given at pH 4 to 6 by:

In DETA-H_2SO_4 - SO_2 solutions,

$$pk_1 = 6.25 + 0.32\,C_D - 0.64\,(C_{SO_4}/C_D) \quad (7)$$

$$pk_s = 4.05 + 0.13\,C_D + 0.92\,(C_{SO_4}/C_D) \quad (8)$$

In DETA - HCl - SO_2 solutions,

$$pk_1 = 7.51 + 0.31\,C_D - 1.20\,(C_{Cl}/C_D) \quad (9)$$

$$pk_s = 2.90 + 0.03\,C_D + 1.03\,(C_{Cl}/C_D) \quad (10)$$

Generally, increasing solution concentration (C_D) increases pk_1, but has little effect on pk_s. Increasing fraction neutralization (C_{acid}/C_D) reduces pk_1 and increases pk_s.

Measurements of pH in 0.4 and 0.8 m DETA neutralized only by dissolved SO_2 were not correlated well by pk_1 and pk_s. The pH data were given instead by the empirical equation:

$$pH = 10.72 - 2.72\,C_D + 1.76\,C_{SO_2} - 3.36\,C_{SO_2}/C_D \quad (11)$$

SO₂ VAPOR/LIQUID EQUILIBRIUM

Steam requirements for simple absorption/stripping are determined primarily by the temperature dependence and the linearity of the vapor/liquid equilibrium relationship. Roberson and Marks [7] used dynamic saturation to measure SO_2 and H_2O vapor pressure over concentrated DETA solutions neutralized with SO_2. The SO_2 vapor-pressure measurements were only accurate above 0.01 bar. We have extended this work to include lower SO_2 vapor pressures and solutions with HCl and H_2SO_4.

At pH values between 3.0 and 5.0, dissolved SO_2 is present primarily as bisulfite, so the SO_2 vapor pressure (P_{SO_2}) is proportional to a_{H^+} and total dissolved SO_2:

$$SO_2(g) + H_2O \rightleftarrows HSO_3^- + H^+$$

$$P_{SO_2} = K\,a_{H^+}\,C_{SO_2}$$

In weak acids the temperature dependence of pH is negligible and the heat of absorption of SO_2 is about equal to the heat of vaporization of water; therefore, the ratio P_{SO_2}/P_{H_2O} is independent of temperature [6]. In DETA solutions the dependence of pH on temperature can be accounted for by taking the ratio $P_{SO_2}/P_{H_2O}^{v}$ to be independent of temperature. The exponent v is expected to be less in the presence of high concentrations of $SO_3^{=}/HSO_3^-$ which reduce the pH temperature dependence.

TABLE 2: pk VALUES FOR DETA–H_2SO_4–SO_2 AND DETA–HCl–SO_2 SOLUTIONS AT 25°C

Concentration (m)			Measured	Measured
DETA	HCl	H_2SO_4	pk_1	pk_s
1.60	—	1.60	6.10	5.23
1.60	—	1.84	6.03	5.23
1.60	—	2.08	5.93	5.43
0.80	—	0.80	5.87	5.17
0.80	—	0.92	5.79	5.20
0.80	—	1.04	5.69	5.48
0.40	—	0.40	5.74	5.03
0.40	—	0.46	5.63	4.97
0.40	—	0.52	5.51	5.35
0.80	1.60	—	5.35	4.99
0.80	1.84	—	5.00	5.26
0.40	0.80	—	5.23	4.94
0.40	0.92	—	4.87	5.28

Experimental Methods

SO_2 vapor pressure was measured by dynamic saturation at 40 to 135°C and by an SO_2 gas sensing electrode at 25°C as in previously reported work on citrate buffers [*4,6*]. The SO_2 electrode was calibrated in solution containing 1.0 m NaOH, 0.5 m citric acid, and 0.05 or 0.2 m SO_2. P_{SO_2}/P_{H_2O} of the calibration solutions was calculated from the correlation given by Rochelle [*4*].

The activity of water, a_{H_2O}, was estimated by a Raolt's law relation:

$$a_{H_2O} = 1.0 - 0.0481\,C_D - 0.0332\,C_{Na} \quad (13)$$

The coefficient for C_D was fitted with the data of Roberson and Marks [*7*]. The coefficient for C_{Na} was derived from data on vapor pressure lowering by NaCl [***14***].

Results

The equilibrium data for DETA-HCl-SO_2 and DETA-H_2SO_4–SO_2 solutions have been correlated in terms of K_D, defined as:

$$K_D = \frac{P_{SO_2}}{(a_{H_2O}P^{\circ}_{H_2O})^{1.75}\,C_{SO_2}10^{-pH}} \quad (14)$$

The pH is taken at 25°C and the exponent 1.75 (v) includes the effect of temperature on pH and on SO_2 vapor pressure. As summarized in Table 3, measured values of the exponent vary from 1.63 to 1.99.

In the absence of HCl and H_2SO_4, the sulfite/bisulfite buffer reduces the favorable temperature dependence of the DETA buffer. Measured values of the exponent v vary from 1.38 to 1.58. Therefore, data for DETA-SO_2 solutions have been correlated in terms of K_{D1}, defined as:

$$K_{D1} = \frac{2.378\ \text{bar}^{-0.25}P_{SO_2}}{a_{H_2O}^{1.75}P^{\circ\,1.5}_{H_2O}\,C_{SO_2}10^{-pH}} \quad (15)$$

K_{D1} is defined so that it is equal to K_D at 25°C.

Table 3 gives average values of K_D and K_{D1} for sets of experiments with equal DETA concentrations. Figure 1 shows that K_D decreases with increasing DETA concentration. This would be expected, since the activity coefficient of bisulfite should decrease at higher ionic strength and because of interaction with DETA cation. The dependence of K_D on DETA concentration is given by:

$$K_D \text{ or } K_{D1} = 5300\,C_D^{-0.29} \quad (16)$$

The correlation of K_D can be used to generate equilibrium curves if pH at 25°C is predicted from the solution composition. Figure 2 gives equilibrium curves using Equations 6, 7, 8, 14 and 16 for 1 m DETA with 1.0, 1.3, and 1.4 m H_2SO_4. The curves are nonlinear and illustrate that capacity for SO_2 absorption can be changed arbitrarily by adding H_2SO_4.

SOLUTION STABILITY

DETA solutions with dissolved SO_2 are subject to thermal degradation in the stripper (80 to 120°C) and oxidation in the absorber (30 to 60°C, 3 to 8% O_2). Disproportionation of dissolved SO_2 to sulfate and thiosulfate or oxidation to sulfate is undesirable because these relatively stable salts must be removed from the system without loss of DETA and because they constitute a waste-disposal problem. DETA degradation will contribute to makeup costs and may give environmentally undesirable waste products. Thermal degradation is especially important because it determines the maximum stripper temperature and places a limit on the reduction of steam consumption that can be achieved by increased stripper temperature.

Disproportionation of sulfite, bisulfite, or SO_2 irreversibly produces sulfate and thiosulfate by the stoichiometry:

$$4HSO_3^- \rightarrow S_2O_3^{=} + 2SO_4^{=} + 2H^+ + H_2O$$

TABLE 3: SUMMARY OF VLE DATA

Solution Composition (m)				
DETA	Other Acid	SO_2	K_D or K_{DI} × 10^{-3} (m^{-1} $bar^{-0.75}$)	$\frac{d \log P_{SO_2}}{d \log P_{H_2O}}$
0.40		0.8–0.9	6.8 ± 1.0	1.50–1.55
0.82		1.4–2.0	5.2 ± 1.7	—
1.0		1.9–2.3	4.3 ± 0.9	1.38–1.58
2.8		6.3	3.6 ± 0.5	—
4.6		9.3	4.4 ± 1.1	1.50
	HCl			
0.26	0.64	0.2	5.9 ± 0.5	1.64
2.7	4.1	2.2	—	1.72
2.7	5.4–7.2	0.1–1.4	2.9 ± 0.7	—
3.0	6.8–7.4	0.6–0.7	3.7 ± 0.9	1.79–1.99
	H_2SO_4			
0.17	0.2	0.2	9.4 ± 1.3	1.68
0.4	0.4	0.04–0.3	9.2 ± 0.9	1.72
1.0	1.3	0.26–0.35	7.2 ± 0.5	1.85
1.2	1.2–1.6	0.2–1.2	6.0 ± 0.6	1.63–1.77
2.6	0.1–0.7	0.1–1.4	3.8 ± 1.3	1.72

This reaction has been observed in the Wellman-Lord and NH_3 absorption/stripping processes, where regeneration is carried out above 100°C [*15*, *16*]. In absorption/stripping with basic aluminum-sulfate solution, Applebey [*17*] observed that thiosulfate catalyzed disproportionation. In a sodium-citrate buffer solution at 70 to 180°C, Rochelle and Gibson [*5*] found that disproportionation had an activation energy of 45 kcal/gmol, a second-order dependence on thiosulfate, and a 1.6-order dependence on H^+, but was independent of dissolved SO_2.

Above 130°C, Rochelle and Gibson [*5*] found that sulfite reacted with citrate to give sulfo-tricarballylic acid. Similar reaction of DETA and sulfite may also occur.

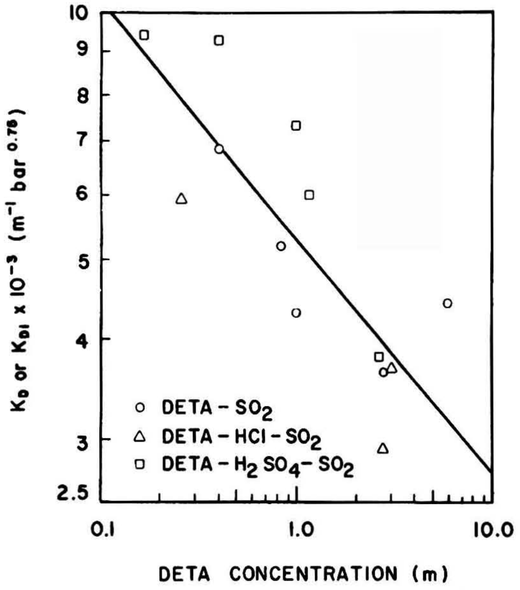

Figure 1. Dependence of K_D or K_{DI} on DETA concentration.

Sulfite oxidation in the absorber is an important side-reaction, but we have not included it in the scope of this work. Oxidation of adipic acid conjugated with sulfite oxidation has been observed in limestone slurry scrubbers [*18*]. Similar degradation of DETA may occur with sulfite oxidation in the absorber.

Experimental Methods

Thermal degradation of DETA/SO_2 solutions was studied using the same apparatus and procedures as used in the study of sodium citrate buffers [*5*]. The solution was held in a stainless-steel reactor at 120 to 165°C for 2 to 75 hours. Intermittent samples were analyzed for sulfite and thiosulfate by iodimetric titration with and without formaldehyde. Final samples from several experiments were analyzed for DETA and other volatile amines by gas chromatography on chromasorb 103 at 190°C.

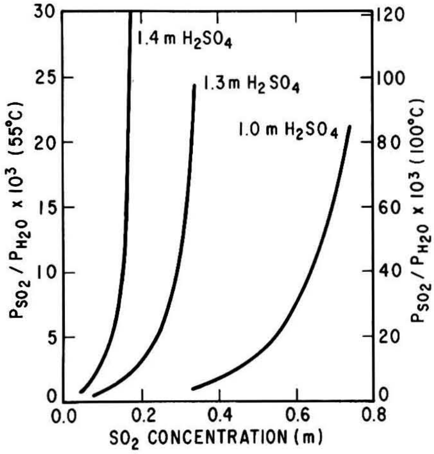

Figure 2. Calculated vapor/liquid equilibria for 1.0 m DETA/1.3 m H_2SO_4.

A single experiment on oxidative degradation was performed in the same apparatus used for study of adipic acid degradation [*18*]. A solution containing 0.5 m DETA and 1.0 m SO_2 was sparged with pure O_2 at 55°C and pH 5.0.

Disproportionation

The rate of SO_2 disproportionation in DETA solutions was correlated as the sum of two parallel reactions, one catalyzed by DETA and one by thiosulfate.

Twenty two experiments were performed with the initial absence of thiosulfate over the following range of conditions:

$[DETA] = 0.16$ to $2.0\ \underline{m}$
$[SO_2] = 0.08$ to $2.6\ \underline{m}$
$[HCl] = 2.6$ to $5.0\ \underline{m}$ (9 experiments)
$[H_2SO_4] = 0.65$ to $1.3\ \underline{m}$ (3 experiments)
$T = 120$ to $165°C$
$pH(25°C) = 2.6$ to 5.5

The rate of SO_2 disappearance (R_{DETA}) was correlated in terms of initial solution composition ($\underline{m}$) by:

$$R_{DETA} = B \cdot e^{-(E_{A1}/RT)} \cdot [DETA]^a \cdot [SO_2]^b \cdot a_{H+}^c \qquad (17)$$

	DETA-HCl-SO_2 and DETA-H_2SO_4-SO_2 Solutions Only	All DETA Solutions
	12 points	22 points
log B	10.33 ± 26%	10.34 ± 19%
E_{A1}(kcal/gmol)	19.0 ± 26%	20.6 ± 18%
a	1.04 ± 40%	0.28 ± 61%
b	0.42 ± 60%	0.96 ± 13%
c	0.68 ± 24%	0.27 ± 23%

The a_H+ term at reaction temperature is estimated for HCl and H_2SO_4 containing solutions by:

$$\log a_{H+} = -pH(25°C) + 1721 \left(\frac{1}{298} - \frac{1}{T}\right) \qquad (18)$$

and for DETA-SO_2 solutions:

$$\log a_{H+} = -pH(25°C) + 1147 \left(\frac{1}{298} - \frac{1}{T}\right) \qquad (19)$$

The standard deviation for the DETA-H_2SO_4-SO_2 and DETA-HCl-SO_2 model is a factor of 1.44. The standard deviation for all 22 data points without thiosulfate is a factor of 1.75.

There were five experiments performed with DETA in the presence of thiosulfate. Four of these used 1 $\underline{m}$ DETA and 1.3 $\underline{m}$ H_2SO_4 with 0.1 to 0.3 $\underline{m}$ SO_2 and 0.05 to 0.1 $\underline{m}$ $Na_2S_2O_3$ at 120 or 135°C. One experiment was performed at 150°C with 2.0 $\underline{m}$ DETA, 5.0 $\underline{m}$ HCl, 0.2 $\underline{m}$ SO_2, and 0.2 $\underline{m}$ $Na_2S_2O_3$. The rate of SO_2 loss attributed to thiosulfate catalysis (R_{Thio}) was calculated as the difference between the total measured rate and the calculated rate attributed to DETA catalysis (R_{DETA}). Disproportionation rates were also measured at 120 to 150°C in 8 solutions containing 2 $\underline{m}$ acetate, 2.6 $\underline{m}$ Na^+, 0.1 to 0.4 $\underline{m}$ SO_2, 0.09 to 0.37 $\underline{m}$ $Na_2S_2O_3$, and 0.6 to 1.8 m Cl^-.

These data in DETA and acetate buffers and previously reported data in citrate and acetate buffers [5] were correlated by the equation:

$$R_{Thio} = Ce^{-(E_{A2}/RT)} [S_2O_3^=]^d a_{H+}^e \qquad (20)$$

$\log C = 13.03 \pm 11\%$
$E_{A2} = 21.6 \pm 10\%$ kcal/gmol
$d = 1.70 \pm 13\%$
$e = 0.54 \pm 16\%$

For citrate and acetate solutions, a_H+ was taken to be 10^{-pH} at 25°C. For DETA solutions it was estimated at reaction temperature by Equation 18.

The standard deviation of the rate prediction for all 24 experiments with thiosulfate is a factor of 1.74. Because it includes more data, this rate expression for thiosulfate-catalyzed disproportionation should be more reliable than that proposed by Rochelle and Gibson [5]. It is similar in form and magnitude to the rate expression for acid decomposition of thiosulfate found by Johnston and McAmish [*19*]:

$$\frac{d[S]}{dt} = k\, a_{H+} [S_2O_3^=]^2$$
$$k = 1.6 \cdot 10^{11} e^{-(16{,}500/RT)}\ \underline{m}^{-2}\ sec^{-1}$$

It also compares well to the rate of reaction of H_2S with thiosulfate measured by Keller [*20*]:

$$\frac{d[H_2S]}{dt} = k\, a_{H+}^{0.5} [S_2O_3^=]^{1.5}$$
$$k = 3.0 \cdot 10^{11} e^{-(16{,}500/RT)}\ \underline{m}^{-1}\ min^{-1}$$

All of these reactions are probably limited by the reaction of thiosulfate with bithiosulfate ($HS_2O_3^-$) to produce bisulfite and a higher monosulfonate [*21*]:

$$HS_2O_3^- + S_2O_3^= \rightarrow HSO_3^- + S_3O_3^=$$

The disproportionation kinetics do not agree well with kinetics for the reaction of thiosulfate and bisulfite at 70°C, which were found to be first order in bisulfite and third order in thiosulfate [22]. We found that R_{Thio} was independent of SO_2 concentration.

The total rate of SO_2 disproportionation (R_{Total}) is given by:

$$R_{Total} = R_{DETA} + R_{Thio} \qquad (21)$$

where R_{DETA} is given by Equation 17 and R_{Thio} by Equation 20.

Sulfite Oxidation

With 1.0 $\underline{m}$ SO_2 and 0.5 $\underline{m}$ DETA at pH 5.0 the initial sulfite oxidation rate was 0.4 $\underline{m}$/hr, which is about the same as the O_2 mass-transfer rate previously determined for the oxidation apparatus [*18*]. The rate of SO_2 oxidation began to decrease at 0.4 $\underline{m}$ SO_2 and was about 0.03 $\underline{m}$/hr at 0.1 $\underline{m}$ SO_2.

DETA Degradation

Final samples from the oxidation experiment and 5 thermal degradation experiments were analyzed by gas chromatography. There was less than 5% loss of DETA in all of the experiments. Ethylenediamine was the only degradation product observed. At 150°C with 0.5 $\underline{m}$ DETA and 1.24 $\underline{m}$ SO_2 it was produced at a rate of 7.1×10^{-3} $\underline{m}$/hr. At 120°C with 1$\underline{m}$ DETA, 1.3 $\underline{m}$ H_2SO_4, and 0.3 $\underline{m}$ SO_2, it was produced at a rate of 1.1 to 1.8×10^{-4} $\underline{m}$/hr. In the oxidation experiment it was produced at a rate of 2.6×10^{-3} $\underline{m}$/hr. In all cases the rate of ethylenediamine production was at least an order of magnitude less than the rate of SO_2 disappearance. It is possible that DETA is degraded by attack of the carbon at the secondary amine to give ethylenediamine and sulfoethylamine:

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 + SO_3^= \rightarrow H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2 + H_2N\text{-}CH_2\text{-}CH_2\text{-}SO_3^-$$

Sulfoethylamine would not be detected by gas chromatography.

DESIGN IMPLICATIONS

The major design variables for simple absorption/stripping are stripper temperature, pH, DETA concentration, and the neutralizing acid. The number of stages in the stripper and absorber and the extent of cross-exchange can also affect system performance. For a given SO_2 removal and flue-gas composition, the primary performance variables are steam consumption, absorbent degradation, and SO_2 absorption capacity. Rochelle [*1*,*23*] has given extensive coverage of process options and design techniques for absorption/stripping processes. In this paper we will use those techniques to evaluate DETA for use in simple absorption/stripping.

The following estimates of steam consumption assume 90% SO_2 removal from flue gas with 3000 ppm SO_2. Unless noted, the absorber is at 55°C and the stripper is at 100°C. The extent of heat exchange between hot lean solution and cold rich solution is assumed to be sufficient to eliminate its effect on the steam requirement. This should be economically feasible if the SO_2 absorption capacity is greater than 0.05 to 0.1 m. Pure steam is used for stripping and there is no reflux in the stripper.

For minimum steam consumption an infinite number of absorber and stripper stages are used with an optimized liquid circulation rate. Ideally, with a linear equilibrium relationship that is independent of temperature, the minimum steam requirement is 51.7 gmol steam/gmol SO_2 removed. Favorable temperature dependence reduces this by a factor of 4.0 for DETA-H_2SO_4-SO_2 and DETA-HCl-SO_2 solutions and a factor of 2.9 for DETA-SO_2 solutions.

An estimate of minimum steam consumption with 1.0 m DETA/1.3 m H_2SO_4 is illustrated in Figure 3. Because of equilibrium nonlinearity, the stripper operating line is tangent to the equilibrium curve. The minimum steam consumption for this case is 23.1 gmol/gmol SO_2. It is 1.80 times greater than the ideal case because of nonlinearity.

Over a range of 0.5 to 1.5 m DETA at inlet pH 4.6 to 5.6 (25°C), the minimum steam consumption varies only from 19 to 24 gmol/gmol SO_2. However, the SO_2 absorption capacity is easily changed by adding or removing acid and varies from 0.04 to 0.4 m. Solution with 0.5 m DETA and only SO_2 gives a higher minimum steam consumption of 32.6 gmol/gmol SO_2, because of reduced temperature effects in DETA/SO_2 solutions.

Actual steam consumption with 3 absorber stages and 6 stripper stages is given in Figure 4. With 1.0 m DETA/1.3 m H_2SO_4 the actual steam consumption is 39.5 gmol/mole SO_2 (11.1 kg/kg). The SO_2 absorption capacity is 0.15 m.

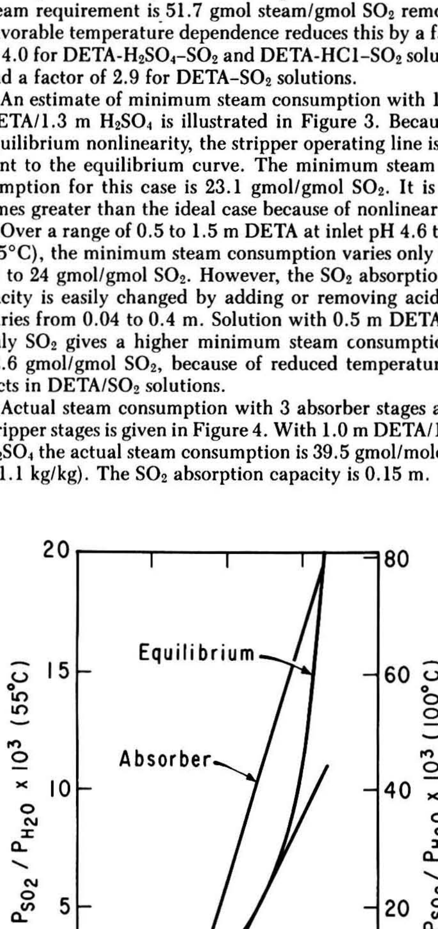

Figure 3. Minimum steam consumption for 1.0 m DETA/1.3 m H_2SO_4, 55°C absorption, 100°C stripping, 90% removal from 3000 ppm SO_2.

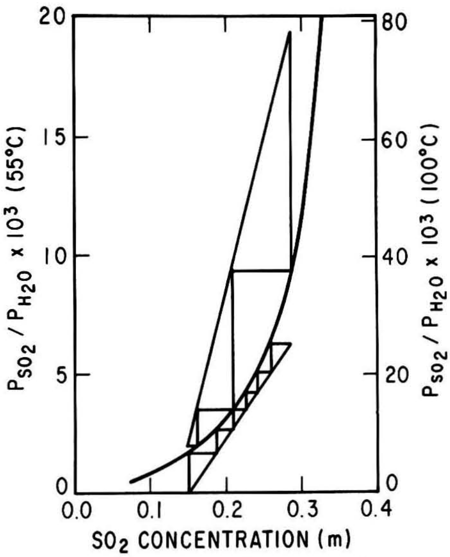

Figure 4. Actual steam consumption for 1.0 m DETA/1.3 m H_2SO_4, 3 stages absorption, 6 stages stripping.

Steam consumption for DETA-H_2SO_4-SO_2 solutions should be sensitive to stripper temperature and very sensitive to absorber temperature. Absorption at 40°C rather than 55°C would reduce steam consumption by a factor of 3.8. Stripping at 120°C rather than 100°C would reduce steam consumption by a factor of 1.7.

The optimum stripper temperature is a tradeoff between steam consumption and sulfite disproportionation. Higher temperature increases disproportionation but decreases steam consumption. Figure 5 gives the calculated range of operating conditions that would give a marginally acceptable rate of disproportionation. The operating temperature can be maximized by increasing pH and minimizing the accumulation of thiosulfate.

In solution containing 1.0 m DETA, 1.2 m H_2SO_4, 0.15 m SO_2, and 0.1 m $S_2O_3^=$ at 100°C, the calculated rate of disproportionation is 4.4×10^{-4} m/hr. With an SO_2 absorption capacity of 0.1 m and a stripper residence time of 1 hour, this corresponds to degradation of 0.44% of the absorbed

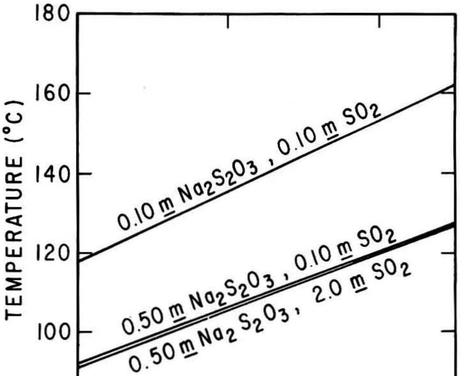

Figure 5. Temperature and pH giving 0.02 m/hr SO_2 disproportionation in 1.0 m DETA.

SO_2. At 120°C the degradation rate would increase to 2.27%, but should still be acceptable.

CONCLUSIONS

1. DETA solutions neutralized by HCl or H_2SO_4 can give 2.2 to 4.0 times better steam consumption for simple absorption/stripping than weak acid buffers such as sodium citrate.
2. DETA solutions neutralized only by SO_2 can give 1.5 to 2.7 times better steam consumption than sodium-citrate solutions.
3. Stripper temperature should be maximized to reduce steam consumption. SO_2 disproportionation will limit stripper temperature to about 120°C and will require purge treatment to control thiosulfate accumulation.

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NOTATION

$a, b, c,$ = Exponents in Equation 17
a_i = Activity of species i, ($\underline{m}$ or m)
B = constant in Equation 17, ($\underline{m}^{l-a-b-c}\ hr^{-1}$)
C = constant in Equation 20, ($\underline{m}^{l-d-e}\ hr^{-1}$)
C_i = concentration of species i, ($\underline{m}$ or m)
C_D = total concentration of DETA species, $\underline{m}$ or m
C_{SO_2} = total dissolved SO_2 ($SO_2 + HSO_3 + SO_3^=$), ($\underline{m}$ or m)
d, e = exponents in Equation 20
E_{A1} = disproportionation activation energy, (kcal $gmol^{-1}$)
E_{A2} = disproportionation activation energy, (kcal $gmol^{-1}$)
f = fraction neutralization, defined dimensionless
ΔH_I = heat of neutralization, $DETAH_2^{+2}/DETAH_3^{+3}$, (kcal $gmol^{-1}$)
ΔH_s = heat of neutralization, $SO_3^=/HSO_3^-$, (kcal $gmol^{-1}$)
K_I = dissociation constant for $DETAH_3^{+3}$, ($\underline{m}$ or m)
k_I = effective dissociation constant for $DETAH_3^{+3}$, ($\underline{m}$ or m)
K_s = dissociation constant for HSO_3^-, ($\underline{m}$ or m)
k_s = effective dissociation constant for HSO_3^-, ($\underline{m}$ or m)
K_D = constant defined by Equation 14, ($m^{-1}\ bar^{-0.75}$)
K_{DI} = constant defined by Equation 15, ($M^{-1}\ bar^{-0.75}$)
m = molality, (gmol solute/kg H_2O)
$\underline{m}$ = molarity, (gmol solute/liter)
m_i = molality of species i, (gmol solute/kg H_2O)
pH = $-\log a_{H^+}$
pK = $-\log K$
P_i = vapor pressure of species i, (bar)
$P^\circ_{H_2O}$ = vapor pressure of pure water, (bar)
R = universal gas constant, 1.987, (cal $°K^{-1} gmol^{-1}$)
R_{DETA} = SO_2 disappearance rate in DETA solutions without thiosulfate, ($\underline{m}\ hr^{-1}$)
R_{Thio} = thiosulfate catalyzed SO_2 disappearance rate, ($\underline{m}\ hr^{-1}$)
R_{Total} = total SO_2 disappearance rate, ($\underline{m}\ hr^{-1}$)
T = temperature, (°K)
v = $d\ ln\ P_{SO_2}/d\ ln\ P_{H_2O}$
$[\,]$ = concentration of charged species, ($\underline{m}$ or m)

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A Promising NO_x-Control Technology

Combustion-modification NO_x-control technology—hope on the horizon for pollution abatement of the emissions from industrial boilers?

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The 1970 Clean Air Act designated oxides of nitrogen (NO_x) as one of the criteria pollutants requiring regulatory controls to prevent potential widespread adverse health and welfare effects. To attain and maintain ambient air quality standards, the act mandated control of new mobile and stationary NO_x sources, each of which emits approximately half of the manmade NO_x nationwide. As shown in Figure 1, industrial boilers represent the third largest contributor to total stationary source NO_x emissions. Indeed, industrial boilers were the origin of approximately 14 percent of all stationary NO_x emissions for the year 1977[*1*].

Since the Clean Air Act, NO_x control techniques have been developed and implemented reducing emisions by a significant amount (20 to 60 percent) for a variety of source/fuel combinations, notably in the utility boiler sector. With increasingly stringent New Source Performance Standards (NSPS) established for utility boilers, the Environmental Protection Agency (EPA) is currently compiling and developing background information on industrial boilers with the intent of proposing NSPS[2]. State and local regulatory developments also point to increasing NO_x control implementation.

Combustion-modification NO_x control technology for coal-, oil-, and natural gas-fired industrial boilers is summarized in this paper. The effectiveness of controls in reducing NO_x emissions and their applicability to industrial boilers are reviewed. Demonstrated or expected operational or environmental impacts are highlighted, and energy and cost impacts are noted. An assessment of the environmental impact was performed for two selected coal-fired boilers to estimate the overall environmental benefit of NO_x control for these units. Information presented in this paper is based primarily on results by Lim *et al.*[3]. A discussion of NO_x formation mechanisms and principles of control is given by Mason *et al.*[4]. The majority of the emissions data evaluated are drawn from References [5] through [*16*].

OVERVIEW OF NO_x CONTROL TECHNIQUES

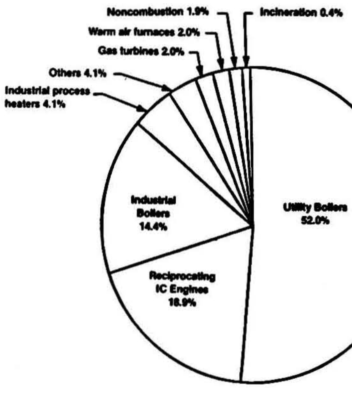
The combustion-modification NO_x controls having possible application to industrial boilers include:

- Low excess air (LEA)
- Staged combustion (SC)
- Low NO_x burners (LNB)
- Flue gas recirculation (FGR)
- Reduced air preheat (RAP)
- Load reduction (LR) or reduced combustion intensity (furnace redesign)
- Ammonia injection (selective noncatalytic reduction)

Ammonia injection, though actually a post-combustion technique, is included here as a process modification because the reducing agent, ammonia, is injected in the boiler proper. Post-combustion flue-gas treatment techniques under development (e.g., selective catalytic reduction) have the potential for even greater NO_x reductions, but at significantly greater capital and operating costs as reviewed by Jones and Johnson[*17*].

Low Excess Air

Reducing the excess air level in the furnace has generally been found to be an effective method of NO_x control for all fuels, reducing NO_x by 5 to 25 percent. In this technique, the combustion air is reduced to the minimum amount required for complete combustion, maintaining acceptable furnace cleanliness and steam temperature.



Total: 10.5×10^9 kg/yr (11.6×10^9 tons/yr)

Figure 1. Distribution of stationary anthropogenic NO_x emissions for the year 1977 (stationary fuel combustion) [1].

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With less oxygen available in the flame zone, both thermal and fuel NO_x formation is reduced. In addition, the reduced airflow reduces the quantity of flue gas released per unit time, resulting in an improvement in boiler efficiency. LEA, being the simplest NO_x control technique with the added benefit of improved boiler efficiency, is often the first technique implemented.

Staged Combustion

Staged combustion, through the use of overfire air (OFA) ports or burners-out-of-service (BOOS), seeks to control NO_x by carrying out initial combustion in a primary, fuel-rich combustion zone, then completing combustion at lower temperatures in a second, fuel-lean zone. The technique involves firing the active burners (or the combustion bed in the case of stokers) more fuel-rich than normal while admitting the remaining combustion air through OFA or inactive burners (BOOS). SC is generally very effective for NO_x reduction and may be used with all fuels with reductions of up to 30 percent.

Low NO_x Burners

Low NO_x burners are generally designed to reduce flame turbulence, delay fuel-air mixing, and establish fuel-rich zones where combustion initially takes place. The longer, less intense flames produced with LNB's, as compared to those of conventional burners, result in lower flame temperatures that reduce thermal NO_x generation. Moreover, the reduced availability of oxygen in the initial combustion zone inhibits fuel NO_x conversion. LNB's represent a developing technology that promises highly effective NO_x control at a relatively low cost, with NO_x reductions of 40 to 60 percent projected.

Flue-Gas Recirculation

Flue-gas recirculation for NO_x control consists of extracting a portion of the flue gas and returning it to the furnace, admitting the flue gas through the burner windbox. FGR lowers the bulk furnace gas temperature and reduces oxygen concentration in the combustion zone. The former effect is probably dominant, since FGR has been found to be most effective in reducing thermal NO_x. FGR has not been found to be an effective control method, considering the major equipment modification involved, for coal and residual oil, fuels for which fuel NO_x often predominates. Indeed, NO_x reductions of only 10 to 15 percent have been found for coal firing, but reductions of 40 to 70 percent have been achieved for distillate oil and gas. Addition of FGR to a boiler is a major modification: the fan, dampers, and controls, as well as possibly having to increase existing fan capacity due to increased draft loss, can represent a large investment.

Reduced Air Preheat

Reducing the amount of combustion preheat lowers the primary combustion zone peak temperature, generally lowering thermal NO_x production as a result. It is an effective technique applicable to the clean fuels: distillate oil and natural gas. However, to prevent severe energy penalties, an economizer should be substituted when possible as a flue gas heat-recovery device. RAP has not been found effective for coal-fired units.

Load Reduction

Reducing combustion intensity generally lowers thermal NO_x formation. Reduced combustion intensity can be brought about by load reduction in existing units and by use of an enlarged firebox in new units. NO_x reduction field test results on industrial boilers have been mixed, on a retrofit basis, but the technique is probably best implemented as an increased furnace plan area in new designs, based on results for new utility boilers.

Ammonia Injection

This technique selectively reduces NO to N_2 and H_2O with injection of ammonia (NH_3) at flue-gas temperatures ranging from 1070 to 1270K (1470 to 1830°F) without a catalyst. However, the method is very temperature-sensitive, with maximum NO_x reductions occurring in a very narrow temperature window around 1240 ± 50K (1770 ± 90°F). Addition of hydrogen can lower and thus extend the effective temperature window. An elaborate NH_3 (and possibly H_2) injection, monitoring, and control system is required. The application of this technique to flue gas from coal combustion has not been demonstrated in the field. Several industrial boilers in California are being fitted with ammonia injection as part of demonstration programs. Control effectiveness is projected to be 40 to 60 percent [*18, 19*]. Ammonia injection is a postcombustion technique under development for possible application after conventional combustion modifications have already ben applied, where additional NO_x reductions are required.

APPLICATION OF CONTROLS TO COAL-FIRED BOILERS

Pulverized Coal

Combustion-modification NO_x controls have been successfully implemented on a limited number of industrial boilers. Representative equipment design types and typical baseline (uncontrolled) NO_x emissions from industrial boilers are listed in Table 1. It should be noted that NO_x emissions are site-specific, dependent on individual boiler/burner design differences, fuel properties, and local combustion conditions. Thus a particular boiler can exhibit an emission level different from the one indicated.

Of seven pulverized coal-fired units tested, baseline NO_x emissions ranged from 174 to 563 ng/J, with most data from 200 to 300 ng/J. No significant correlation of emission levels with (pulverized coal) boiler type (i.e., tangential versus wall-fired), coal properties, or operating conditions was evident from the limited data. For example, Figure 2 shows that the fuel nitrogen content has no significant effect on NO_x emissions from coal-fired industrial boilers. Although undoubtedly fuel NO_x emissions increase with increasing fuel nitrogen-content, the emissions increase is not proportional; furthermore, such effects are often overshadowed by boiler design and operating parameters. Indeed, Figure 2 shows that the data for pulverized coal and spreader stoker units are clustered in the 200- to 300-ng/J heat input range, while other stoker types are clustered in the 100- to 200-ng/J range, all independent of fuel nitrogen content. All these units were generally operating at normal excess air levels.

Table 2 lists the combustion modifications applicable to pulverized coal-fired industrial boilers. Combustion modifications for which no actual data exist for the industrial boiler size range have also been included, based on utility boiler experience which is much more extensive. Clearly, industrial boiler-control test data are limited.

Low Excess Air

Low excess air operation is a relatively simple technique to implement. It is applicable to all boiler types and requires only reducing airflow to the burner windbox. However, in a multiburner unit, modifications to the windbox may be necessary to improve air distribution to individual

TABLE 1. REPRESENTATIVE INDUSTRIAL BOILERS AND TYPICAL BASELINE NO$_x$ EMISSION LEVELS

Fuel	Boiler Type	Typical Size (Heat Input Capacity) MW (10^6 Btu/hr)	Average NO$_x$ Baseline Emission Level ng NO$_2$/J (lb/10^6 Btu)
Pulverized Coal	Single Wall and Tangential	59 (200)	285 (0.663)
Stoker Coal	Spreader	44 (150)	265 (0.616)
	Underfeed	9 (30)	150 (0.349)
	Chain Grate	22 (74)	140 (0.326)
Residual Oil[a]	Firetube	4.4 (15)	115 (0.267)
	Watertube	44 (150)	160 (0.372)
Distillate Oil	Firetube	4.4 (15)	70 (0.163)
	Watertube		
	Without air preheater	29 (100)	55 (0.128)
	With air preheater		90 (0.208)
Natural Gas	Firetube	4.4 (15)	40 (0.093)
	Watertube		
	Without air preheater	29 (100)	45 (0.105)
	With air preheater		110 (0.255)

[a] Includes No. 5 and No. 6 fuel oils.

burners during LEA operation. Lowering excess air can reduce the safety margin for complete combustion. Hence, installation of an oxygen-trim system may be necessary, in addition to the normal airflow controllers. Nevertheless, boiler efficiency gains with LEA should offset any additional hardware costs, and thus make LEA the most attractive NO$_x$ control technique for first implementation (5 to 25 percent NO$_x$ reduction). Figure 3 shows the result of LEA tests on representative coal-fired industrial boilers. The slopes of the data bands indicate the relative effectiveness of LEA on each equipment category. It is seen that LEA is about equally effective for each category.

Staged Combustion

Staged combustion with OFA and LEA represents the best demonstrated, available control option for pulverized coal-fired industrial boilers, potentially reducing NO$_x$ emissions by up to 30 percent. The LEA and OFA control system has a primary advantage over the other control systems because of its commercial availability and its effectiveness. The cost of the system is not prohibitive when OFA ports are designed as a part of new boilers. In addition, careful operation of staged air injection is not expected to seriously affect emissions of other criteria pollutants.

Burner stoichiometries in the range of 100 to 110 percent would be adequate to achieve a 20-percent NO$_x$ reduction. At these stoichiometry levels, oxidizing atmospheres would prevail in the furnace, thus minimizing concern over possible furnace slagging and boiler-tube wastage. However, achieving more stringent NO$_x$ control with combined LEA and OFA may require that burner stoichiometries be reduced below 100 percent in some cases. This low burner stoichiometry level would cause reducing atmospheres in parts of the furnace, thus creating the potential for corrosion of water tubes, especially when firing high-sulfur coal[21]. Generally, boiler manufacturers do not recommend burner operation with stoichiometry below 100 percent, primarily because of increased corrosion potential. Another potential adverse impact is that additional excess air may be required to ensure complete combustion, resulting in a decrease in boiler efficiency. However, experience with utility boilers indicates that these potential problems can be overcome with proper design and implementation[21]. Indeed, a recent 30-day, continuous monitoring test of SC with LEA, at varying reduced boiler loads, demonstrated a 30-percent NO$_x$ reduction with no adverse operational impacts[16].

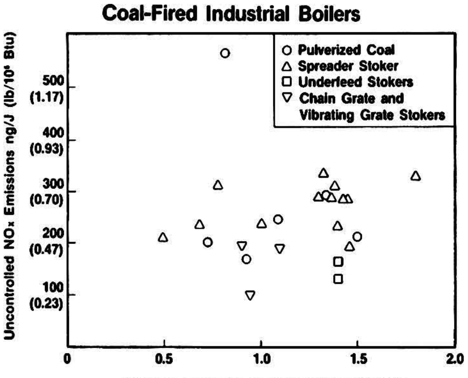

Figure 2. Effect of fuel nitrogen on NO$_x$ emissions from coal-fired industrial boilers.

Burners-out-of-service is the other technique that can be used to achieve staged combustion. It is primarily considered for retrofit application. However, it is not a favored technique because of several limitations:

- Extensive engineering and testing on an individual boiler basis is required to determine the optimal BOOS pattern
- Selection of an effective BOOS pattern is sometimes not possible because pulverizers may serve burners located on two separate levels. The most effective BOOS pattern often involves only the top level of burners on air only.
- In many cases, burners/pulverizers that operate during BOOS cannot handle increased coal flow, necessitating a significant reduction in the boiler steam rating (e.g., 20-percent derate)
- Potential increased slagging and corrosion

Low NO$_x$ Burners

Because of the possible operational problems associated with SC, a number of low NO$_x$ burner designs are under development by commercial firms, with 40 to 60 percent NO$_x$ control projected. An advanced design under study is a distributed fuel-air mixing concept being developed by the Energy and Environmental Research Corp. for the EPA[22]. Field testing and application is scheduled for late 1982, with a target NO$_x$ level of 86 ng/J (0.2 lb/10^6 Btu)[22, 23].

TABLE 2. COMBUSTION-MODIFICATION NO_x CONTROLS FOR PULVERIZED COAL-FIRED INDUSTRIAL BOILERS

Control Technique	Description Technique	Number of Industrial Boilers Tested	Effectiveness of Control (Percent NO_x Reduction)	Range of Application	Commercial Availability/ R&D Status	Comments
Low Excess Air (LEA)	Reduction of combustion air	7	0-25 (avg. 9)	Excess oxygen reduced to 5.2% on the average	Available	Added benefits of technique include increase in boiler efficiency, limited by increase in CO. HC and smoke emissions.
Burners Out of Service (BOOS)	One or more burners on air only. Remainder firing fuel-rich.	2	27-39 (avg. 33)	Applicable only for boilers with minimum of 4 burners	Available. However, extensive engineering work necessary prior to implementation.	Limited by the number of burners available. Load reduction required in most cases. Possible increased slagging, corrosion.
Overfire Air Injection (OFA)	Secondary air from OFA ports above fuel rich firing burners		5-30	Burner stoichiometry as low as 100%	Commercially offered but not demonstrated for industrial size boilers	Requires installation of OFA ports, etc. Possible increased slagging, corrosion.
Flue Gas Recirculation (FGR)	Recirculation of flue gas to burner windbox		0-20	Up to 25% of the flue gas recirculated	Not offered because relatively ineffective	Requires installation of FGR ducts, fan, etc. Can cause combustion instability. Burner windbox may need extensive modifications.
Low NO_x Burner (LNB)	New burner designed utilizing controlled air-fuel mixing		40-60	Prototype LNB limited to size ranges above 29 MW (100×10^6 Btu/hr)	Still in the development stage. Prototype LNB available from major boiler mfrs.	Active R&D efforts underway
Ammonia injection	Injection of NH_3 in convective section of boiler		40-60	Limited by furnace geometry. NH_3 injection rate limited to 1.5 NH_3/NO.	Commercially offered but not demonstrated	Elaborate NH_3 injection, monitoring and control system required. Possible load restrictions on boiler and air preheater fouling by ammonium bisulfate.
Reduced Load	Reduction of fuel and air flow to the boiler.	6	Varies from 45% reduction to 4% increase in NO_x	Applicable to all boilers. Load can be reduced to 25% of capacity.	Available now but not implemented because of adverse operational impacts	Load reduction often not effective because of increase in excess O_2. Best implemented with increase in furnace size for new boilers.

In some applications, LNB's may have several advantages over other combustion modifications such as SC with OFA or BOOS. For example, one utility boiler manufacturer claims that LNB's will maintain the furnace in an oxidizing environment, minimizing slagging and reducing the potential for furnace corrosion when firing high-sulfur coal[*24*]. Also, more complete carbon utilization may be achieved due to better coal-air mixing in the furnace. Finally, lower oxygen levels may be obtained with all the combustion air admitted through the burners[*21*].

Since the burners generally alter the flame configuration, care must be taken when applying the burners to existing boilers. For instance, some LNB's have a longer flame length. Such burners can be installed only in those boilers large enough to avoid cold-wall impingement. Once developed, however, low NO_x, coal-fired burners for industrial boilers could become the best control system because of the expected lower cost, higher NO_x reduction capability, and other operational advantages over SC.

Ammonia Injection

If additional control over and above boiler/burner modifications are needed (e.g., to meet stringent local regulations), ammonia injection is a commercially offered technique. The technique has yet to be demonstrated on coal-fired boilers and is generally several fold more costly than conventional combustion modifications. In addition, as a developing technology, there are several potential implementation and operational problems that need to be resolved:

- Optimal effectiveness for noncatalytic reduction of NO by NH_3 occurs over a very narrow temperature range; hence, the precise location of NH_3 injection ports is crucial
- Since the temperature profile in a boiler changes with load, NO_x control with NH_3 may dictate load restriction
- Emissions of NH_3 and byproducts

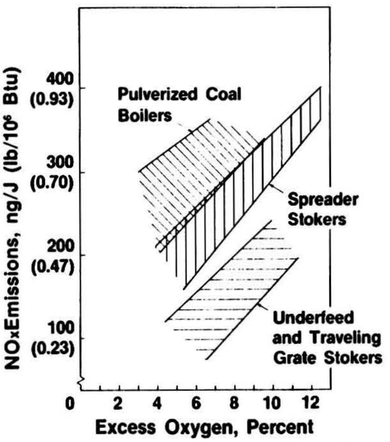

Figure 3. Effect of excess oxygen on NO$_2$ emissions from coal-fired boilers.

- Possible boiler equipment fouling by ammonium sulfates

However, the major strengths of the technique are its potential for high NO$_x$ removal (40 to 60 percent), and its applicability is an additional control that can be combined with conventional combustion techniques for large NO$_x$ reductions [*18*, *19*].

Stoker Coal

NO$_x$ emission from stokers are generally lower than those from pulverized coal. These lower emissions have been attributed to the lower combustion intensity and to the partial staged combustion that naturally occurs during combustion on fuel beds[25].

As illustrated in Figure 2, NO$_x$ emissions from spreader stokers tend to be higher than those from other stoker designs. The coal in a spreader stoker boiler burns partly in a suspended state and partly on a moving or vibrating grate. The combustion of coal in the suspended state apparently causes NO$_x$ emissions to be generally higher than for other stoker types that feed and combust coal directly on a moving grate. In addition, the higher heat-release rates of spreader stokers probably also contribute to high NO$_x$ emissions.

Four methods have been used to modify stoker coal combustion to reduce NO$_x$ emissions. These methods are 1) reduced undergrate air or LEA, 2) OFA, 3) reduced heat input, and 4) RAP. Of these methods, only LEA firing has been demonstrated to be widely effective. Table 3 summarizes the performance and limitations of each of these techniques.

Low Excess Air

Low excess air firing represents the only widely effective NO$_x$ control technique for coal-fired stokers. OFA is generally a design feature of all stokers and is controlled independently from undergrate air. LEA tests performed in the field consisted of reducing the undergrate airflow while maintaining the OFA flow close to normal operation.

A series of EPA field tests of 17 stokers indicate that the excess oxygen levels at baseline operating conditions averaged about 9 percent. During LEA tests, the average excess oxygen level was reduced to 6.4 percent. Such reduction lowered NO$_x$ emission levels approximately 10 percent for each 1-percent reduction in excess oxygen. Figure 3 illustrates this trend. Indeed, data from an ongoing EPA-DOE-ABMA field test program involving 11 relatively new design stokers operating near the lower excess air level tend to support this general trend[*15*].

Fuel combustion with lowest possible levels of excess air assures maximum boiler efficiency unless the air is decreased to the point where unburned carbon losses are greatly increased. From the limited amount of data it can be tentatively generalized that if the airflow is maintained such that the excess oxygen level is approximately above 6 percent, no serious operational or emission problem should result. Of course, this generalization would require verification. Indeed, the minimum excess oxygen level for a particular boiler could be higher than 6 percent. NO$_x$ emission reductions of about 5 to 25 percent and increases in boiler efficiency of 1 percent can be expected with LEA, provided fuel burnout does not change during the process.

Staged Combustion

One of the reasons NO$_x$ emissions from stokers is lower than those from pulverized coal-fired boilers is the partial staged combustion nature of combustion of fuel beds[*26*]. Volatile matter leaves the fuel bed as the coal is fed into the grate and burns above the bed level. The solids are subsequently burned with lower combustion intensity.

An increased staged combustion effect beyond what seems to occur naturally in the stoker furnace seems difficult to obtain. However, augmented staged combustion control can be effected by increasing air injection above the fuel bed through the OFA ports and reducing the undergrate airflow.

A reduction of 10 to 25 percent in NO$_x$ has been achieved by this method without increasing CO emissions. However, most stokers have OFA ports originally designed for use as smoke-control devices. Therefore, the location or orientation of the OFA ports may not be the optimum to achieve best NO$_x$ reductions. The current EPA-DOE-ABMA field program has found little success with OFA on existing units[*15*].

The OFA method suffers from the same potential problems as LEA because reduced undergrate airflow is absolutely necessary to achieve any staging effect. Therefore, limitations applicable to the technique of LEA such as grate overheating, corrosion, and clinker formation can also limit the application of the staged combustion technique. An ongoing EPA-sponsored program is examining advanced stoker designs, including use of OFA for NO$_x$ control[27].

Ammonia Injection

Ammonia injection is potentially applicable, although it has not yet been demonstrated on an industrial stoker. The boiler geometry and the flue-gas temperature profile in a stoker should permit the implementation of the NH$_3$ injection process in a similar manner as for a pulverized coal-fired unit. Indeed, the discussion on performance and limitations of ammonia injection as noted earlier for pulverized coal firing is also applicable to stokers.

APPLICATION OF CONTROLS TO OIL- AND GAS-FIRED BOILERS

Combustion-modification NO$_x$ controls have been successfully implemented on a limited number of oil- and gas-fired boilers, as for coal-fired units. Table 4 summarizes the performance characteristics of potentially applicable controls. As noted earlier, low excess air firing is the only demonstrated control technique applicable to all industrial boilers. Figures 4 and 5 give graphical presentations of the excess air test results for these units. Although the test data of Table 4 indicates that LEA is about equally effective on a percentage basis for oil and natural gas (about 11 percent NO$_x$ reduction), Figure 4 shows that absolute NO$_x$ reductions are greater for the higher nitrogen, heavier fuels. This is, of course, expected because LEA is effective in reducing both fuel and thermal

TABLE 3. COMBUSTION-MODIFICATION NO_x CONTROLS FOR STOKER COAL-FIRED INDUSTRIAL BOILERS

Control Technique	Description of Technique	Number of Industrial Boilers Tested	Effectiveness of Control (Percent NO_x Reduction)	Range of Application	Commercial Availability/ R&D Status	Comments
Low Excess Air (LEA)	Reduction of air flow under stoker bed	24	5-25	Excess O_2 limited to 5-6% minimum	Available now but need R&D on lower limit of excess air	Danger of overheating grate, clinker formation, corrosion, and high CO emissions
Staged Combustion (LEA + OFA)	Reduction of undergrate air flow and increase of overfire air flow	5	5-25	Excess O_2 limited to 5% minimum	Most stokers have OFA ports as smoke control devices but may need better air flow control devices	Need research to determine optimal location and orientation of OFA ports for NO_x emission control. Overheating grate, corrosion, and high CO emission can occur if undergrate airflow is reduced below acceptable level as in LEA.
Reduction Load (LR)	Reduction of coal and air feed to the stoker	13	Varies for 49% decrease to 25% increase in NO_x (average 15% decrease)	Has been used down to 25% load	Available	Only stokers that can reduce load without increasing excess air. Not a desirable technique because of loss in boiler efficiency.
Reduced Air Preheat (RAP)	Reduction of combustion air temperature	1	8	Combustion air temperature reduced from 473K to 453K	Available now if boiler has combustion air heater	Not a desirable technique because of loss in boiler efficiency
Ammonia Injection	Injection of NH_3 in convective section of boiler		40-60 (from gas- and oil-fired boiler experience)	Limited by furnace geometry. Feasible NH_3 injection rate limited to 1.5 NH_3/NO.	Commercially offered but not yet demonstrated	Elaborate NH_3 injection, monitoring, and control system required. Possible load restrictions on boiler and air preheater fouling by ammonium bisulfate.

NO_x in the heavier fuels. Number 2 distillate oil and natural gas produce primarily thermal NO_x. Figure 5 shows, as expected, that low excess air firing is more effective for boilers with air preheat because LEA would reduce the amount of preheated air; hence lowering combustion intensity and reducing NO_x formation.

Residual Oil

Baseline NO_x emissions from residual oil-fired firetube boilers are relatively low, averaging 115 ng/J (Table 1). Low excess air operation should lower emissions by about 10 percent and also increase boiler efficiency. The same caution about possible increased CO and hydrocarbon emissions discussed for coal firing under low excess air applies here also. Low NO_x burners or staged combustion are the preferred alternatives if additional control is necessary. However, neither one has been demonstrated for the firetube boiler design. Developing low NO_x burners may become the first control choice after LEA because of their potential for high NO_x reduction with the lowest boiler operational impact.

The generally larger watertube boilers with higher NO_x emissions (160 ng/J average) will also need the same controls: low excess air, low NO_x burners, and staged combustion. Staged combustion is a demonstrated technique for the large multiburner watertube boilers. However, if developing low NO_x burners are successful and achieve about a 50 percent NO_x reduction, down to 86 ng/J (0.2 lb/10^6 Btu), they should prove more cost effective. The only other alternative for stringent control is ammonia injection. Although demonstrated and in limited commercial operation for oil and gas firing in Japan, this control system represents a several-fold more costly alternative for NO_x reduction than the other two systems. In addition, operational problems and potential emissions of NH_3 and by-products may cause environmental concern.

It should be noted that the above-discussed controlled emission levels for residual oil firing may be difficult to achieve for boilers firing high nitrogen content fuel (e.g., greater than 0.3 weight percent nitrogen). Indeed, Figure 6 indicates a possible trend of increasing total NO_x emissions with fuel nitrogen content, unlike the behavior exhibited by coal-fired boilers. A possible explanation may be the following: 1) the fractional conversion of fuel nitrogen to fuel NO_x increases with decreasing fuel nitrogen content, and 2) residual oil generally has a much lower fuel nitrogen content than does coal[9].

It should also be noted from Figure 6 that NO_x emissions from residual oil-fired boilers appear to be independent of combustion air preheat. This is expected because reduced air preheat is primarily effective for reducing thermal NO_x, but fuel NO_x dominates for the heavy oil.

TABLE 4. COMBUSTION-MODIFICATION NO_x CONTROLS FOR OIL- AND GAS-FIRED INDUSTRIAL BOILERS

Control Technique	Description of Technique	No. of Boilers Tested	Effectiveness of Control (Percent NO_x Reduction)			Range of Application	Commercial Availability/ R&D Status	Comments
			Residual Oil	Distillate Oil	Natural Gas			
Low Excess Air (LEA)	Reduction of combustion air	22 residual oil boilers, 7 distillate oil boilers and 28 natural gas boilers	0 to 28 (11 average)	0 to 24 (11 average)	−71 to 83 (Average 10)	Generally excess O_2 can be reduced to 2.5-3.0% representing 2.5-3.0% drop from baseline	Method and control equipment available	Added O_2 benefits included increase in boiler efficiency. Limited by increase in CO, HC, and smoke emissions.
Staged Combustion (SC)	Fuel-rich firing burners with secondary combustion air ports downstream of burner(s) in the direction of the gas path	3 residual oil boilers, 1 distillate oil boiler and 3 natural gas boilers	20 to 50	17 to 44	5 to 46	70-90% burner stoichiometries can be used with proper installation of secondary air ports	Technique is applicable on package and field-erected units. However not commercially available for all design types.	Best implemented on new units. Retrofit is probably not feasible for most units especially packaged ones.
Burners Out of Service (BOOS)	One or more burners on air only. Remainder firing fuel rich.	8 residual oil boilers and 3 natural gas boilers	10 to 30	N/A	17 to 44	Applicable only for boilers with minimum of 4 burners. Best suited for square burner pattern with top burner or burners out of service. Only for retrofit application.	Available. Retrofit requires careful selection of BOOS pattern and control of air flow.	Retrofit often requires boiler derating unless fuel delivery system is modified.
Flue Gas Recirculation (FGR)	Recirculation of portion of flue gas to burners	1 distillate oil boiler, 2 residual oil boilers and 3 natural gas boilers	15 to 30	58 to 73	48 to 86	Up to 25-45% of flue gas recycled. Can be implemented on all design types except ones equipped with ring gas burners.	Available. Requires extensive modifications to the burner and windbox.	Best suited for new units. Costly to retrofit. Possible flame instability at high FGR rates. Most effective on watertube boilers.
Flue Gas Recirculation Plus Staged Combustion	Combined techniques of FGR and staged combustion	Only one package watertube boiler	25 to 53	73 to 77	76	Max. FGR rates set at 25% for distillate oil and 20% for residual oil	Combined techniques are still at experimental stage. Needs more R&D.	Retrofit may not be feasible. Best implemented on new units. No added benefit of SC to FRG performance for gas firing. Combined methods are not additive in their effect.
Load Reduction (LR)	Reduction of air and fuel flow to all burners in service	17 residual oil-fired boilers, 7 distillate oil-fired boilers and 21 natural gas-fired boilers	33% decrease to 25% increase in NO_x	31% decrease to 17% increase in NO_x	32% decrease to 83% increase in NO_x	Applicable to all boiler types and sizes. Load can be reduced to 25% of maximum.	Available now as a retrofit application. Better implemented with improved firebox design.	Technique not effective when it necessitates an increase in excess O_2 levels. LR possible implemented in new designs as reduced combustion intensity (enlarged furnace plan area).
Low NO_x Burners (LNB)	New burner designs with controlled air/fuel mixing and increased heat dissipation.	Large number tested in Japan	20 to 50	20 to 50	20 to 50	New burners described generally applicable to all boilers. More specific information needed.	Commercially offered but not demonstrated	Specific emissions data from industrial boilers equipped with LNB are lacking
Ammonia Injection	Injection of NH_3 as a reducing agent in the flue gas.	5 (4 Japanese installations, 1 domestic)	40 to 70	40 to 70	40 to 70	Applicable for large package and field-erected watertube boilers. May not be feasible for firetube boilers.	Commercially offered but not demonstrated	Elaborate NH_3 injection, monitoring and control system required. Possible load restrictions on boiler and air preheater fouling when burning high sulfur oil.
Reduced Air Preheat (RAP)	Bypass of combustion air preheater	2 residual oil-fired boilers and 2 natural gas-fired boilers	5 to 16	NA		Combustion air temp. can be reduced to ambient conditions (340K)	Available. Not implemented because of significant loss in thermal efficiency.	Application of this technique on new boilers requires installation of a alternate heat recovery system (e.g., an economizer)

Distillate Oil and Natural Gas

NO_x emissions from distillate oil and natural gas combustion are primarily from thermal NO_x formation. The relatively low uncontrolled baseline NO_x emissions from combustion of these fuels (Table 1) should permit achievement of very low controlled NO_x levels. These control levels can in most cases be met with commercially available combustion modification techniques. The preferred control systems are low excess air, reduced air preheat, flue gas recirculation, and low NO_x burners (under development), in that order, lowering NO_x down to about 65 ng/J (0.15 lb/10^6 Btu). Distillate oil- and natural gas-fired boilers not equipped with air preheaters (all firetubes, some watertubes) generally exhibited significantly lower average NO_x emissions than those with preheaters, irrespective of boiler heat input capacity, as shown in Figure 7. Although Figure 7 would seem to indicate a general trend of higher NO_x emissions with increasing boiler capacity, the trend is probably due to factors other than capacity *per se:* design differences such as firetube systems for the smaller boilers and watertube systems for the larger, and air preheaters with the larger units as well. Figure 7 shows that bypassing an existing preheater substantially reduces NO_x (shown for natural gas, though similar behavior is expected for distillate oil). Those boilers without air preheat should be able to reach 43 ng/J (0.1 lb/10^6 Btu) with just flue-gas recirculation, while air preheater-equipped boilers may require combined reduced air pre-

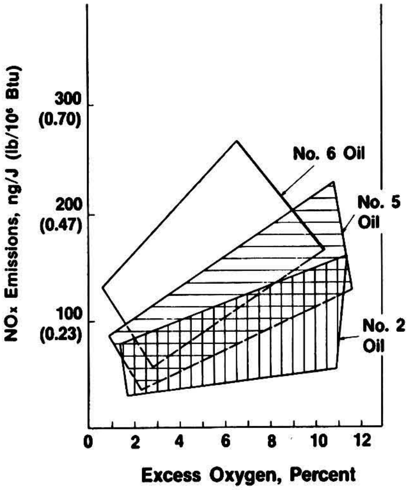

Figure 4. Effect of excess oxygen on NO_x emissions from distillate and residual oil-fired boilers.

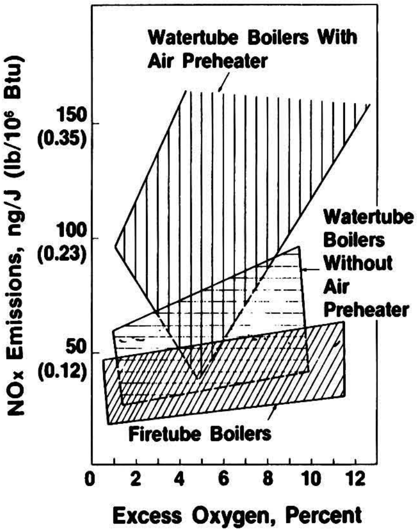

Figure 5. Effect of excess oxygen on NO_x emissions from natural gas-fired boilers.

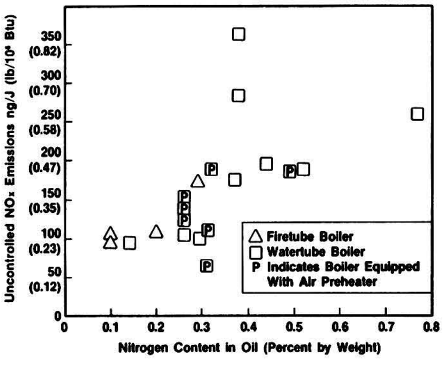

Figure 6. Effect of fuel nitrogen content on NO_x emissions from residual oil-fired industrial boilers.

heat and flue-gas recirculation. Figure 8 illustrates the high effectiveness (40 to 75 percent NO_x reduction) of flue-gas recirculation for clean fuels (distillate oil and natural gas).

ENERGY IMPACT

Of the NO_x control methods available, LEA is the most fuel-efficient. LEA should be used with most control methods to increase thermal efficiency and reduce NO_x emissions. In general, combustion-modification NO_x controls should only have a minor energy impact, usually less than 0.5 percent increase in energy consumption. In fact, with proper boiler design and control implementation, it might even be possible in some cases to significantly lower NO_x emissions and use less energy. The postcombustion NO_x control techniques under development are expected to increase energy usage by less than 1 percent[*17*].

COST IMPACT

The primary contributions of combustion-modification controls to steam cost changes are the equipment modification costs and changes in thermal efficiency and fan power demand. In general, combustion-modification controls should be cost-effective means of control for industrial boilers, raising steam costs only 1 to 2 percent in most cases. However, the initial investment required, especially for smaller boilers, may be a large fraction of the cost of the boiler itself, up to 25 percent when controls are installed on a new boiler. Retrofit control costs, highly site-specific, could be two to three times higher.

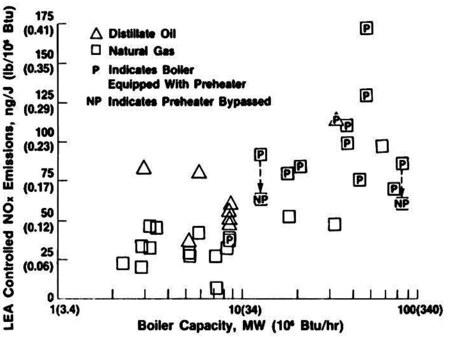

Figure 7. Effect of combustion air preheat and boiler capacity on NO_x emissions from distillate oil- and gas-fired industrial boilers.

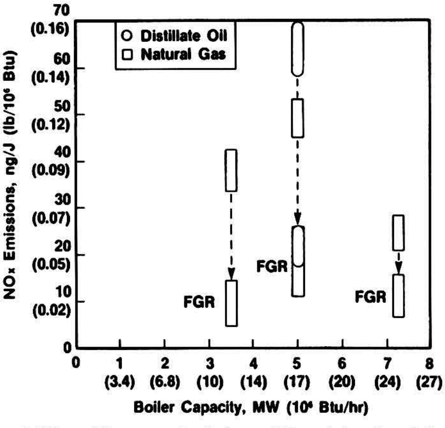

Figure 8. Effect of flue-gas recirculation on NO_x emissions from industrial boilers.

The postcombustion control techniques, because of higher capital equipment, raw material, and energy requirements, are significantly more costly. Ammonia injection is several-fold more costly than conventional combustion modifications, while flue-gas treatment techniques are about an order of magnitude higher than combustion modifications. However, post combustion controls are the only near-term option if extremely high NO_x reductions are required (e.g., 90 percent).

Environmental Impact

To help quantify the potential change in the environmental impact of an industrial boiler that switches from baseline to low NO_x firing, a source analysis model SAM IA[28] was applied to the effluent data from the two stoker coal-fired industrial boilers tested in this study. EPA has been developing a series of source-analysis models to define methods of comparing emission data to environmental objectives, termed Multimedia Environmental Goal (MEG's)[29]. The model selected for the level of data detail obtained from the industrial boiler tests was designed for rapid screening purposes. As such, it includes no treatment of pollutant transport or transformation. Goal comparisons employ threshold effluent-stream concentration goals.

For purposes of screening pollutant emissions data to identify species requiring further study, a Discharge Severity (DS) is defined as follows:

$$DS_i = \frac{\text{Concentration of Pollutant i in Effluent Stream}}{\text{DMEG of Pollutant i}}$$

The DMEG (Discharge Multimedia Environmental Goal) value, a threshold effluent concentration, is the maximum pollutant concentration considered safe for occupational exposure. When DS exceeds unity, more refined chemical analysis may be required to quantify specific compounds present.

To compare waste-stream potential hazards, a Total Weighted Discharge Severity (TWDS) is defined as follows:

$$\text{TWDS} = (\Sigma_i\ DS_i) \times \text{Mass Flow Rate}$$

where the Discharge Severity is summed over all species analyzed. The TWDS is an indicator of output of hazardous pollutants and can be used to rank the needs for controls for waste streams. It can also be used as a preliminary measure of how well a pollutant control, say a combustion-modification NO_x control, reduces the overall environmental hazard of the source.

The tests performed were both cooperative efforts with the EPA-DOE-ABMA field program on stoker emissions and efficiency improvement[*15*]. Site A was a traveling grate spreader stoker with a steam capacity of 38 kg/s (300,000 lb/hr) while Site B, also a spreader stoker, can produce 25 kg/s (200,000 lb/hr). Both boilers were tested in the baseline (normal) operation and low NO_x firing modes. The Site A low NO_x condition was increased overfire air at the same overall excess air level (actually LEA firing) as baseline. The Site B low NO_x mode was low excess air firing.

Environmental Test Results

Table 5 shows the results of the SAM IA evaluation of the flue gas composition data from both Sites A and B. Emission rates are given in References [*13*] and [*14*]. Results are presented for uncontrolled operation (baseline) and controlled operation (low NO_x). The table shows MEG category DS for each firing condition for those components with DS greater than 1 in either test. DS values shown were calculated from air/health-based DMEGs.

The results presented in Table 5 show that NO_x and SO_2 are potentially the most hazardous flue species. The sum of the DS values for these two species comprises over 70 percent of the stream Total Discharge Severity (TDS). The DS for SO_2 fluctuates with day-to-day fuel sulfur content, masking the effects of the reduction of the NO_x DS with the application of NO_x control in the case of the Site A results. For Site B results the DS for SO_2 drops in the low NO_x mode so that stream TDS decreases with NO_x-control application since NO_x DS decreases significantly. Other species of potential concern include CO, SO_3 (vapor), and several trace elements. The sixfold increase in SO_3 DS recorded for the Site A boiler control is not attributed to NO_x control but to the accuracy of the analytical technique used to measure SO_3. With the exception of carboxylic acids for Site A, no organic category had a DS greater than one for either boiler.

Table 6 shows stream DS for each stream under each firing mode tested. The flue-gas stream dominates the potential hazard of the source, with a WDS over two orders of magnitude larger than any other stream. In addition, the WDS's for the ash streams generally remain relatively constant with firing mode. Thus, changes in flue gas WDS will elicit corresponding changes in total source WDS. So it is concluded that the NO_x controls tested reduce total source potential hazard in the absence of sulfur emissions which are dependent on the fuel and not on the NO_x control.

General Comments on Environmental Impact

Based on a review of the emissions data from the two stoker coal-fired boilers tested in this program and published data from other coal-, oil-, and gas-fired industrial boilers, no serious environmental impacts are expected from applying combustion-modification controls. How-

TABLE 5. FLUE GAS DISCHARGE SEVERITY: SITES A & B

		Discharge Severity Site A		Discharge Severity Site B	
Component	MEG Category	Baseline	Low NO_x (OFA)	Baseline	Low NO_x (LEA)
NO_x	47	70	58	68	38
SO_2	53	63	85	39	23
CO	42	6.3	12	1.4	0.88
SO_3 (vapor)	53	5.8	35	1.9	1.6
Be	32	1.9	0.049	0.60	0.13
As	49	1.6	3.5	18	20
Fe	72	1.1	1.9	0.40	0.13
Carboxylic acids	8	1.0	1.8	—	—
Ti	41	0.34	3.7	0.0092	0.0082
Cd	82	0.61	1.7	0.12	0.52
Pb	46	0.38	1.2	0.0080	0.0033
Total stream		154	206	168	114

TABLE 6. WEIGHTED DISCHARGE SEVERITY (kg/s): SITES A & B

Stream	Site A Baseline	Site A Low NO_x (OFA)	Site B Baseline	Site B Low NO_x (LEA)
Flue gas	6,600	7,900	7,160	3,640
Bottom ash	15	16	—[a]	7.7
Mechanical collector hopper ash	1.7	1.8	50	5.5
ESP hopper ash	5.3	2.6	1.9	3.7
Total source	6,620	7,920	7,210	3,660

[a] Bottom ash samples not taken for baseline test.

ever, more field testing is required to quantify and establish that statement. The limited field test data on incremental emissions indicate that pollutant emissions other than NO_x are generally unaffected by proper implementation of preferred combustion-modification NO_x controls. Emissions of CO, unburned hydrocarbons, organics, and SO_2 are largely unaffected. There may be a possible, slight decrease of sulfate and particulate emissions; there also could be slight shifts in trace-metal partitioning. However, all these potential effects appear to be quite secondary compared to the overall reductions in NO_x emissions with the proper application of controls.

CONCLUSIONS

NO_x controls have been applied only to a limited extent in the industrial-boiler sector. An exception is low excess air operation, which is often implemented for boiler efficiency gains. The general trends highlighted in this report are meant to be only guidelines; there will certainly be exceptions, and much research and development work remains to be done before NO_x-control technology is well characterized for the wide diversity of industrial boiler design and equipment types.

However, it can be generally concluded that currently available combustion-modification technology is capable of moderate reductions (10 to 25 percent) for coal- and residual oil-fired boilers, while major reductions (40 to 70 percent) are possible for distillate oil- and gas-fired units with minimal adverse operational or environmental impacts. Advanced techniques under development, such as low NO_x burners and ammonia injection, are potentially capable of more efficient operation and/or additional reductions.

EPA is currently sponsoring several field test programs demonstrating combustion modification NO_x controls for industrial boilers. These programs include identification of optimal combustion conditions for 11 stoker coal-fired boilers, sponsored jointly with the Department of Energy and ABMA[*15*], and field demonstrations of a commercial low NO_x burner for both oil and gas firing[*30*]. The results from these studies should help fill some of the data gaps identified in this study. In addition, several other field tests of these and other combustion controls are underway, including 30-day continuous monitoring programs[*30*]. The results of these and other test programs should be monitored and incorporated in future updates of the assessment of combustion modification NO_x controls.

ACKNOWLEDGMENTS

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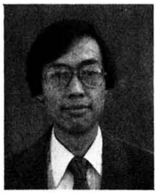

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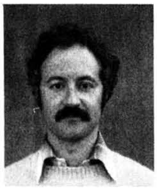

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The Random-Walk Advection and Dispersion Model (RADM)

A sophisticated new model is applied to evaluation of SO_2 pollution at locations in California, Alaska, and North Dakota.

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Stochastic techniques for describing atmospheric dispersion are conceptually simple and attractive, but require a sophisticated data base to provide the required level of input regarding the structure of turbulence and dispersion processes. The stochastic approach is typically formulated in terms of a probability distribution of certain outcomes for a given system of fluid units. For applications of practical concern, the fluid unit is defined to be orders of magnitude larger than the mean free path of the fluid molecules, but small enough to provide adequate resolution of the smallest length scale of interest. Such a fluid unit may be referred to as a fluid "parcel". The interaction between these fluid parcels can be expressed in stochastic terms from a knowledge of the structure of turbulence and dispersive processes. In practical applications, the structure of these processes is often inadequately known and phenomenological descriptions are employed to characterize the dispersive transport. Variations of this approach to the analysis of transport and dispersion of scalar quantities have been employed by Hotchkiss and Hirt [1], Hall [2], Joynt and Blackman [3], Ahlstrom and Foote [4], Watson and Barr [5], Lamb *et al.* [6], Reid [7], and Patterson *et al.* [8].

This paper outlines the basic components, input data requirements, and evaluation of the Random-Walk Advection and Dispersion Model (RADM). The mathematical formulation of RADM is independent of the problem-specific input. As a result, the external algorithms that calculate the required input parameters, such as the wind-field and dispersion coefficients required for atmospheric applications of the program, determine the temporal and spatial scales of the problem. RADM is presently structured to utilize input data and compute atmospheric pollutant concentrations on a spatial scale of 10 to 200 km.

BASIC MODEL COMPONENTS AND SPECIFICATION OF INPUTS

The problem of transport of parcels by advection and dispersion can be represented simply as a series of random walks [9]. Each of these random walks is composed of a deterministic advection component and a random dispersion component as shown in Equation (1):

$$x_t - x_o = \int_{t_o}^{t} U(x_{t'}, t']dt' + n_r\left(\int_{t_o}^{t} 2K(x_{t'},t')dt\ '\right)^{1/2} \qquad (1)$$

where x_o is the initial parcel location, U is a mean velocity vector defined over a suitable time interval, K is a diffusion coefficient also defined over a suitable time interval, and n_r is a normally distributed random number with a mean value of zero and a standard deviation of unity.

For a rigorous application of the random-walk method, the net parcel displacement must be calculated by integration of Equation (1). However, with U and K as arbitrary functions of space and time, it is not always possible to obtain a closed-form solution to this equation. For suitably small time steps, it often proves adequate to assume that the mean velocity and the random components can be separately calculated and linearly superposed. This is the assumption that is employed in the present version of the random-walk method.

In the application of RADM, both U and K are assumed to be externally specified inputs. These inputs may be obtained from field data, laboratory studies, analytical solutions, numerical simulations,or other such means. RADM is a completely Lagrangian model that continuously tracks the motion of a statistically large number (5,000 to 10,000) of arbitrarily released parcels; it is free of any imposed grid. The specification of of U and K, however, may be made on an appropriate grid and a technique specified to calculate inter-grid point values.

The diffusion coefficients used in RADM are computed using a technique described in McRae *et al.* [10]. The technique relies on similarity theory, employing local values of friction velocity, u_* , mixing depth, Z_i, Monin-Obukhov length, L, surface roughness, z_o, and atmospheric stability. The velocity vectors are computed using an analogous methodology which is described in Goodin and McRae [11].

EVALUATION AND APPLICATION

The RADM has been employed for simulating a number of problems with known analytical solutions as well as those utilizing field data (Runchal, *et al.* [12]; Runchal et al. [16]). The subsequent sections of this paper briefly describe two recent evaluation studies that used field data (Goodin, *et al.* [13]; Dames & Moore [14) and one application of the model (Lou and Richmond [15]).

Evaluation of RADM in the San Francisco Bay Area

The purpose of this study was to understand the relationships between SO_2 emissions and $SO_2/SO_4^=$ air quality in the Bay Area as well as to analyze the impacts of natural gas curtailment and proposed SO_2 emissions regulations on ambient air quality. The study area is shown in Figure 1. The majority of the SO_2 sources are located in the Carquinez Straits which are enclosed by a rectangular box in the figure.

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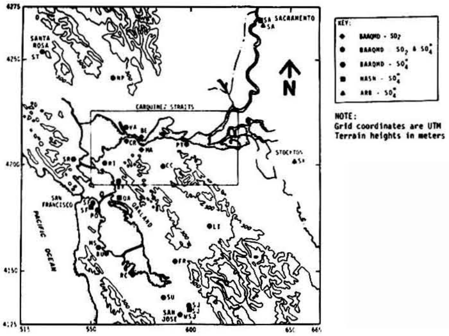

Figure 1. Locations of SO_2 and $SO_4^=$ monitors in the San Francisco Bay area.

Periods suitable for modeling were selected with respect to seasonal distribution and type of flow regime. Four modeling periods, encompassing approximately 10 days of extreme air quality, were selected for study. Two were northeasterly, winter flow regimes; one was a southeasterly, winter regime, and one was a westerly, summer flow regime.

Twenty-four hour averaged emissions from each of the approximately 100 major sources (>12 tons/year) of SO_2 in the Bay Area were provided for each modeling period by the Bay Area Air Quality Management District (BAAQMD) based on information supplied by the source owner. The smaller, distributed-source emissions (small industry, home heating, ships, etc.) were input as emissions per unit area.

Meteorological data required for the study were obtained from the BAAQMD and also from the National Climatic Center, Asheville, North Carolina. The required input data consisted of:

- Cloud cover and insolation;
- Deposition velocity for SO_2;
- Average conversion rate of SO_2 to $SO_4^=$;
- Hourly air temperature in the region of the major sources;
- Average surface roughness and topographic height specified on the scale of 5 km;
- Mixing depth on the scale of 5 km for each hour; and
- A three-dimensional wind field (horizontal components only) on the scale of 5 km for each hour.

Following calculation of the impacts from source emissions, the sulfate background concentrations for each modeling period were determined. This spatially variable background concentration was calculated by RADM from known sulfate concentrations specified at the boundaries of the region. These concentrations were transported into the region by the period-specific wind fields.

Figure 2 shows a plot of computed versus measured $SO_4^=$ concentrations for all four modeling periods. The mean residual concentration was $-0.35\mu g/m^3$ (0.01 pphm as SO_2) which indicates slight overprediction. The mean measured $SO_4^=$ concentration was 6.43 $\mu g/m^3$. The computed correlation coefficient was 0.70 and the slope and intercept of the regression line were 0.71 and 2.06, respectively. This correlation coefficient is comparable to those obtained by other investigators (e.g., Duewer *et al.* [*17*]. The error bars on the observed concentrations were provided by BAAQMD (Levaggi [*18*]. The other lines on the figure indicate the ideal fit and the ± percent accuracy bounds corresponding to the worst-case limits of uncertainty of model input data.

Evaluation of RADM in Port Valdez, Alaska

The purpose of this study was to determine whether the region was in compliance with the National Ambient Air Quality Standard (NAAQS) for SO_2; EPA's previous calcu-

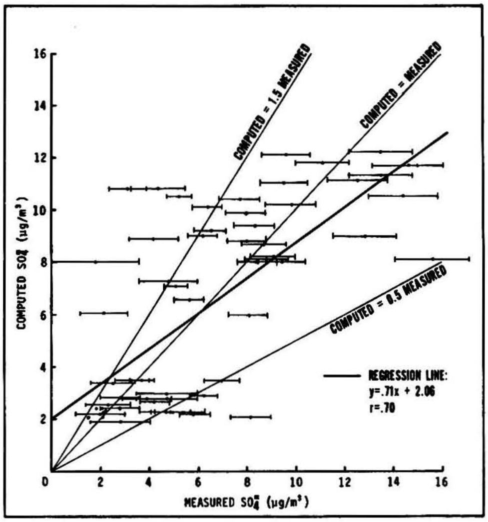

Figure 2. Comparison of measured and computed $SO_4^=$ concentrations from four modeling periods spanning 12 days during 1975 to 1977 in the bay area.

lations using the VALLEY Model had indicated that the region was exceeding those standards. The primary sources of SO_2 were emissions from supertankers and related land-based facilities at Jackson Point. The region of interest is indicated in Figure 3.

Meteorological conditions that are conducive to pollutant buildup in this region are: light winds in the eastern basin area, cool drainage winds in the western basin area resulting from the glaciers, and surface inversion or shallow mixed layers (approximately 200 meters) throughout the basin.

Selection of the individual episodes for model validation was based on several criteria including: relatively high SO_2 levels at one or more monitoring locations, the availability of necessary tanker information for emission estimates, and the number of valid surface SO_2 measurements. Five days with high SO_2 levels were eventually selected for modeling.

The compilation of the emission inventory relied mainly on information provided by Alyeska Pipeline Service Co. However, as many sources of data as possible were used in order to accurately portray the SO_2 emissions during these periods. Data used included tanker size, berth number, and amount and duration of deballasting and cargo loading. For some tankers, the arrival and departure times, fuel sulfur content, and/or amount of fuel used at berth were also available. Emissions data for other sources including

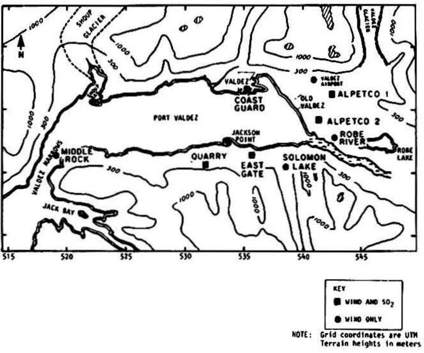

Figure 3. Locations of meteorological and air-quality monitors in the Valdez basin.

boilers, tugboats, waste-gas incinerators, trash incinerators, and diesel generators were also included in the inventory.

The meteorological data requirements for this study were very similar to those in the San Francisco Bay area. The major differences were that the conversion rate of SO_2 to $SO_4^=$ and deposition velocity were less important because the residence times of parcels in the basin were shorter. The grid size for construction of the wind fields, diffusivity fields, and mixing depth fields was 1.6 km in this study. It is also important to note that less meteorological data were available for this study than in the San Francisco Bay area study, but the dimensions of the Port Valdez region were also smaller.

Figure 4 shows a plot of measured versus computed SO_2 concentrations for the five days in 1978 that were modeled. Multiple data points at the same location on the graph are not shown. The slope of the least-squares line was 0.69 with an intercept of 6.62. The correlation coefficient was 0.74. The magnitudes of errors in the measured data were not available.

The correlation coefficient was higher in this study than in the previous study for a number of reasons. There were a number of hours when no SO_2 was measured or computed (origin of graph); the pollutant of interest was emitted as a primary pollutant; the residence times of air parcels in the region were short, and the receptors were generally close to the sources of SO_2.

Application of RADM in Western North Dakota

RADM was used to assess the impacts on the existing sulfur dioxide air quality in North Dakota of a proposed coal-to-methanol conversion facility. The relative distances of the proposed facility and other sources to EPA Class I areas in North Dakota mandated modeling techniques capable of simulating long-range transport and diffusion. As travel times increase, spatial and temporal variations of meteorological conditions considerably alter a plume's trajectory and dispersion characteristics. Similarly for these plumes, removal and transformation mechanisms become increasingly important. As a result, the RADM was deemed very appropriate for an analysis of this type. This project did not involve model validation because sulfur dioxide is not routinely measured at the low levels that are permitted for the Class I increment.

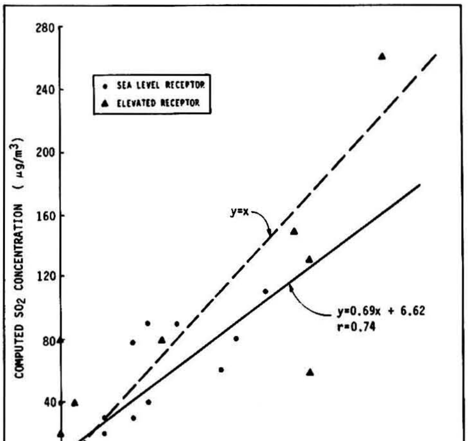

Figure 4. Comparison of measured and computed SO_2 concentrations for two sea-level and one elevated receptor spanning 5 days in 1978 in the Valdez basin.

In order that the total impact on nearby Class I area could be assessed, all major SO_2 emission sources within the state of North Dakota and the eastern portion of Montana were included in the study. This encompassed sources within about 180 km of the proposed facility. The inventory used was compiled from data made available by the State of North Dakota. Since area sources were assumed to be small they were not included in the study.

An important aspect of the study was the construction of the three-dimensional flow field. The data base consisted of surface winds and Pasquill stabilities from five stations and upper-air data containing mixing heights and winds from three stations. The wind input arrays included 10 vertical levels, the lower level derived from the surface wind stations and upper levels computed from the 3 upper-air stations.

The results of the RADM calculations indicated that the proposed facility would comply with all Class I increments for SO_2. It should also be noted that the major part of increment consumption would be due to other sources. The meteorological conditions that led to high 3-hour predictions were associated with transient fumigation. The high 24-hour concentration values were due to persistent flow aligned with the major sources upwind of the northern unit of Theodore Roosevelt National Park.

SUMMARY AND CONCLUSIONS

The mathematical framework of a stochastic, random-walk model has been developed to simulate transport under conditions of complex advection and dispersion. The framework allows for inclusion of other physical transport processes, such as chemical reaction, radioactive decay, particle drag, settling, and deposition.

The mathematical model, called RADM, is completely Lagrangian and is based upon the superposition of a random dispersive displacement on a deterministic advective displacement. Its structure is not dependent on the form of the physical and empirical input and other problem-specific features. The model is especially simple to apply and possesses a number of advantages over the commonly employed grid-based models. These are summarized below:

- RADM has no imposed spatial grid system and is thus completely free from the restrictions of grid-related numerical stability, accuracy, and false diffusion that are commonly encountered in Eulerian models employing finite difference or finite element techniques.
- The only time and space scales of concern for RADM are the physically relevant ones such as those for advection or diffusion. No artificial grid-related scales are present. Thus, the time and space resolution is easily tailored to the availability of input or requirements for output. For example, with RADM the pollutant concentrations need only be computed at locations and time intervals specified by the user.
- The RADM methodology is well suited for dealing with the turbulence characteristics of the wind field. It is easily employed with either the usual K-theory approach or the statistical approach to turbulent dispersion.
- When modeling the movement of a plume, RADM can resolve its location and concentration more accurately than an Eulerian grid model. The representation of a plume in an Eulerian grid depends on the relationship between cell size and plume dimensions.
- RADM is well suited for modeling pollutant transport under complex meteorological conditions such as stagnation, flow reversal, or flow in regions of complex terrain. This is because each parcel is transported by the local meteorological conditions that it encounters as it moves across the region of interest.

A number of comparisons between the RADM simulations and analytical solutions, as well as field data, have been performed. The RADM results, in all cases, have compared very favorably with the measured concentrations.

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Organic Emission Control Devices

The environmental-control engineer's handy guide to preliminary selection of the best device for a special organic emission.

James W. Blackburn, IT Enviroscience, Inc., Knoxville, Tenn. 37923

The air-pollution control engineer has options to specify a number of different control devices for organic emissions. Specification and design of most organic air-pollution control devices require a knowledge of the specific organics present in an air emission, because different organic compounds have different physical properties that have major effects on the system design.

In a recent contract for the EPA (Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry, Contract No. 68-02-2577) IT Enviroscience studied a variety of air-pollution control devices in use in the synthetic organic chemical industry. These devices included thermal oxidation, flares, the use of emissions as fuels, carbon adsorption, absorption, and condensers. A control device evaluation (CDE) report was prepared on each of these control devices. These reports have been published in two volumes of the final report for that program [*1*-*7*].

These CDE reports focused on analyzing the basic design of each control device for a wide range of flows and VOC concentrations. The important VOC physical properties for design were studied and, where possible, the range of variation of these properties was established. The design techniques and assumptions were stated in these reports, and a variety of systems were designed spanning the flow and VOC concentration range of interest, which were ~500 to 100,000 ft³/min and 100 ppm$_v$ to 100% VOC concentration (~850 to 170,000 m³/hr).*

Capital cost curves for each of the unit operations in the control device were generated by contacting vendors and using a consistent method to analyze the costs. A summary of the capital cost estimating procedure is shown in Table 1. Annual costs were determined from the control-device designs. The unit costs shown in Table 2 use consistent unit costs. Since these unit costs were determined early in the four-year contract, they are somewhat low today. However, as they are consistent from control device to control device, the economic evaluations represent an ideal tool for comparative evaluation.

The control-device evaluation reports deal with each technology in some detail. Capital and annual costs are presented in the CDE reports for a variety of control device alternatives. This paper seeks to offer a more simplified summary of the technical and economic ramifications of selecting an organic air-pollution control device. In doing so, additional assumptions are made. The tables and charts in this paper should be considered as only a preliminary selection tool. For instance, if the VOC concentration and flowrate of the emission is known, the charts would be used to determine the most and least costly control devices and the technical feasibility of their use. Control devices that are not technically feasible or are too expensive can be rejected and the remaining control devices can be further considered by using the CDE reports, vendor contacts, and other more detailed sources.

TECHNICAL CONSIDERATIONS

In general, technical considerations include the important properties of the VOC that limit the application, maximum capacities related to technical or practical reasons, VOC removal efficiencies, energy effectiveness, and other factors. A discussion of these considerations follows.

Combustion Control Devices

Thermal oxidation at conventional (1200 to 2200°F or 650 to 1200°C) and high temperatures (2200 to 3000°F or 1200 to 1650°C), catalytic oxidation, flares, and the use of emissions as fuels are all used to control VOC emissions. In all combustion-control devices the heat content of the waste gas is the most significant VOC property that relates to system design. The heat content is in turn determined by the VOC's heat of combustion. Because the heats of combustion vary so widely (50,000 to 2,000,000 Btu/lb-mole of organic or 116,200 to 4,646,000 J/g-mole), knowing the VOC concentration alone is inadequate. As can be seen in Figure 1, an emission with a heat content of 12.5 Btu/ft³ (466 kJ/m³) could vary in VOC concentration between about 0.2 to 5 mole % of VOC. Alternatively, a waste gas with, say, 1 mole % VOC varies in heat content between 2 to 55 Btu/ft³ (74.5-2050 kJ/m³). A waste gas with a heat content of 2 Btu/ft³ (74.5 kJ/m³)would be a lean gas and significant supplementary fuel would be required for combustion. A waste gas at 55 Btu/ft³ (2050 kJ/m³) could support combustion on its own with little supplementary fuel. So for a 1 mole % of VOC stream, significant cost differences are expected.

Heat content of the waste gas also determines the minimum combustion temperature of the combustion device. A waste gas with about 60 and 80 Btu/ft³ (2230-2980 kJ/m³) could support at combustion about 1400 to 1600°F (760 to 870°C), respectively. A waste gas containing 100 Btu/ft³ (3720 kJ/m³) would only burn at 1600°F (870°C) if it were diluted with air or another gas. This implies that high-heat content waste gases achieve higher combustion temperatures. A heat content of 100 Btu/ft³ (3720 kJ/m³) will burn at a temperature of about 1900°F (1040°C) and 200 Btu/ft³ (7450 kJ/m³) would achieve about 2200°F (1200°C).

Conventional thermal oxidation is defined as operating at temperatures between 1200 and 2200°F (650 to 1200°C). Most experts agree that at temperatures over 1600°F (870°C) and at a residence time of 0.5 sec, most organic compounds achieve over 99% removal. This is a controver-

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*All volumetric flowrates cited in this paper are at the standard conditions of 0°C and 101.3 kPa.

TABLE 1. FACTORS USED FOR ESTIMATING TOTAL INSTALLED COSTS

A = Major Equipment Purchase Cost Plus 0.1 to 0.35 Allowance	
Installation Costs	
Foundations	0.06A + $100 X number of pumps
Structures	0.15A (no structures) to 0.30A (multideck structures)
Equipment Erection	0.15A to 0.30A (depending on complexity)
Piping	0.40A (package units) to 1.10A (rat's nest)
Insulation	0.06A or 0.15 X piping (normal) to 0.30 X piping (bulk hot or cold)
Paint	0.05A
Fire Protection	0.01A to 0.06A (depending on requirements)
Instruments	0.10A to 0.30A or 0.01A to 0.25A + $50,000 to $300,000 for process control computer
Electrical	0.15A or 0.05A + $500 per motor
B = Base Cost	A + Sum of Installation Costs
Sales Tax	0.025A + 0.025B
Freight	0.16A
Contractor's Fees	0.30 (B-A)
C = Total Contract	B + Taxes, Freight, and Fees
Engineering[a]	0.01C to 0.20C
Contingencies[b]	0.15C
D = Process Unit Installed Cost	C + Engineering + Contingencies
E = Total Subestimates	Sum of semidetailed subestimates (buildings, site development, cooling towers, etc.). Each subestimate should include taxes, freight, fees, engineering and contingency, and should be escalated to date of expenditure for that cost component. Engineering costs, contingencies, and escalation factors for these subestimates will vary according to the type of job.
F = Total Project Cost	D + E

[a] Includes cost from capital project teams, process engineering, engineering, purchasing, and other support groups.

[b] Contingency should not be applied to any cost component that has been committed by either purchase order or contract.

TABLE 2. ANNUAL COST PARAMETERS

Operating factor	8760 hr/yr
Fixed costs	
Maintenance labor plus materials, 6%	29% installed capital
Capital recovery, 18%[a]	
Taxes, insurances, administration charges, 5%	
Operating labor	$15/hr
Utilities	
Electric power	$0.03/kWh
Steam	$2.50/million Btu
Natural gas and energy recovery credits	$2.00/1000 scf
Cooling water	$0.10/1000 gal
Wastewater treatment	$0.25/1000 gal + $0.10/lb of BOD
Carbon adsorption cost (5-yr replacement)	$1.17/lb

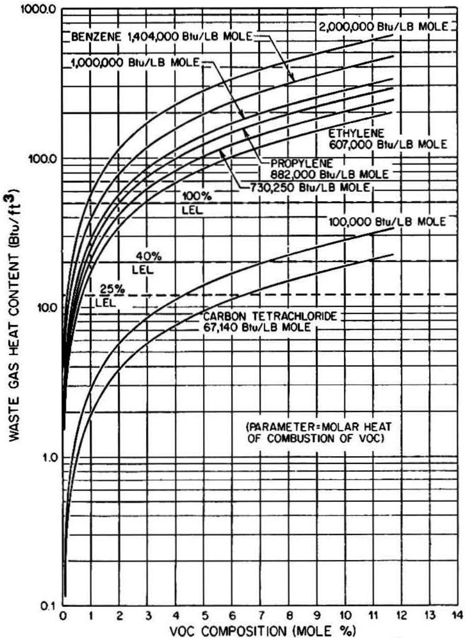
[a] Based on 10-year life and 12% interest.

Conversion factors: $/kWh × 0.2778 = $/MJ
$/million Btu × 9.480 × 10^{-4} = $/MJ
$/1000 ft^3 × 35.31 = $/1000 m^3
$/lb × 2.203 = $/kg

sial area and work is now going on to better estimate the destruction efficiency as functions of time and temperature.

Waste gases with low heat contents (less than 12.5 Btu/ft^3 or 466 kJ/m^3) can be burned in catalytic oxidizers. These devices achieve high destruction efficiencies at temperatures lower than conventional thermal oxidizers (<1200°F or 650°C). However, catalytic oxidizers cannot be used for control of all VOC. Waste gases containing compounds such as phosphorous, bismuth, lead, arsenic, antimony, mercury, iron oxide, tin, silicon, zinc, sulfur, or halogens may poison the catalyst and render the control device ineffective. Catalytic oxidizers can only be used for the subset of emissions with low heat contents and for waste gases containing no catalyst poisons.

High-heat content waste gases can be burned in thermal oxidizers, flares, or boilers if adequate air-pollution control for noxious combustion products is supplied. If the VOC in the organic emission contains an element which leads to a noxious combustion product (S, Cl, Br, etc.), a scrubber is often required. The most common example of this case is the control of chlorinated organics. Cl_2 or HCl is generated



Conversion Factors: Btu/ft^3 x 37.24 = kJ/m^3
Btu/lb-mole x 2.323 = J/g-mole

Figure 1. Relationship between waste gas heat content, VOC composition, and VOC molar heat of combustion

as a combustion product of chlorinated organics. Chlorine is difficult to remove by scrubbing and the oxidizer is operated at high temperatures to fully convert the Cl_2 to HCl. The flue gas generated at high temperatures can then be scrubbed with water in an absorption column to generate an HCl solution. Halogenated organics require both high-temperature thermal oxidizers and scrubbers to fully solve the air-pollution problem.

Flares are generally used for high-heat content waste gases with intermittent flow characteristics. Waste gases with heat concentration as low as 50 to 60 Btu/ft^3 (1860 to 2230 kJ/cubic liters) can be considered for control by flares but much higher heat contents are normally seen in waste gases fed to flares. VOC destruction efficiencies are controversial, but can be in excess of 99% under appropriate conditions.

Existing boilers can be used to control high-heat content waste gases. Corrosion of the boilers and the potential of boiler downtime and maintenance must be considered because these factors are functions of the corrosive nature or slagging tendency of the VOC combustion products. Often the destruction efficiency in a boiler cannot be determined in advance, although the destruction efficiencies can match those of thermal oxidizers.

Combustion of waste gases at moderate and low heat contents is highly energy intensive. Much of the annual cost of such a device is related to the fuel required to burn the waste gas. This heat is lost in hot flue gases unless heat recovery is included. Two types of heat recovery are in common practice—recuperative heat recovery and waste-heat boilers. Recuperative devices transfer heat from the hot flue gas to heat the cool waste gas and combustion air. These devices are limited because of materials of construction considerations to applications less than or equal to 1600°F (870°C) combustion temperature. Even at this temperature, alloys are used to reduce corrosion problems.

Waste-heat boilers can be utilized at any combustion temperature and can recover heat by generating steam with the hot flue gas. The maximum heat recovery possible when using a waste-heat boiler depends on the final temperature of the flue gas after heat recovery, assumed to be 500°F (260°C).

Carbon Adsorption

Two specific properties of the organic compounds are important in the design of carbon adsorption systems. These are the VOC molecular weight and the actual operating capacity of the adsorption system for the VOC. VOC concentration is related to these properties by the following equation:

$$\text{VOC Concentration} = \frac{(\text{Carbon Requirement})(\text{Operating Capacity})}{\text{VOC Molecular Weight}} \times 0.00359$$

The units used are mole fractions for the VOC concentration, lb of carbon/1000 ft^3 for carbon requirement, and lb of VOC/100 lb of carbon for operating capacity. (Carbon requirement expressed as kg of carbon/1000 m^3 can be converted to lb/1000 ft^3 by dividing by 16.03.) For a given concentration, then, the carbon requirement varies directly with molecular weight and inversely with the operating capacity. This study assumes that molecular weights of organic vapors vary between 50 and 150 with 100 being typical and operating capacities vary between 5 and 20 with 7 being typical.

Carbon adsorption may require pretreatment to contend with conditions such as high waste-gas temperatures, high humidity, entrained liquids and solids, and high-boiling organics. Waste-gas temperatures should be less than 100°F (38°C) or the system capacity will be lowered. Relative humidity of the waste gas should be less than 50%. Excursion beyond 50% relative humidity will also reduce the capacity. Dilution air may be used to control temperature and humidity, but a larger system will be necessary.

Entrained solids and liquids pose different problems. Solids tend to plug the bed since carbon itself acts as a filter. Prefiltration is recommended. Liquids can load on the carbon, resulting in lower capacity for removal of the vaporized organics. Entrained liquids must be removed.

High-boiling organics will load on the bed and will not be volatilized during steam regeneration. The result will be cumulatively lower capacities and short carbon lifetimes. High-boiling organics should be avoided.

Carbon adsorption systems are normally designed for waste gases below 25% of the lower explosion limit (LEL) of the VOC for safety reasons and design related considerations. Twenty-five percent of the LEL for organics in air-containing waste gas translates to a heat content of 12.5 Btu/ft^3 (466 kJ/m^3). As noted earlier in the combustion-device discussion, this implies a range of VOC concentrations from about 0.2 to 9 mole % of VOC. However, compounds at the high-concentration range have low heats of combustion and are generally highly oxygenated or halogenated organics. The heat of adsorption released during loading of high concentrations of organics increases the bed temperature and decreases the capacity. Waste gas VOC concentrations should be limited to less than 2 mole % to minimize this factor. This limitation will allow design at the 25% LEL level for all VOC except organics with very low heat contents.

A properly designed carbon adsorption system generates a gas with very low VOC concentration. The actual effluent concentration varies, depending on the effectiveness of the prior regeneration cycle. The assumption used in the CDE report was that 70 ppm_v VOC and 12 ppm_v VOC could be achieved at steam usages in regeneration of 0.3 and 1.0 lb of steam/lb of carbon (g of steam/g of carbon) respectively. If the waste gas is greater than 7,000 ppm_v VOC, then removal efficiencies should be greater than 99% for both cases. (This assumes steady-state operation. VOC concentration surges or transient VOC components with low operating capacities can adversely affect the removal efficiency.)

Carbon adsorption is not generally a destructive control technology. VOC removed can be recovered and reused. Sometimes this offers an advantage over the destructive combustion technologies.

Absorption

Absorption systems can be designed to control waste gases over the entire VOC concentration range. (Although concentrations less than 200 to 300 ppm_v usually favor other control devices.) A primary design consideration that strongly affects the system design is the gas-liquid equilibrium between the VOC in the waste gas and in the liquid used for the absorption fluid. For VOC where the slope of the equilibrium line is low, absorption can be a very efficient and low-cost control device. As the slope increases, the removal efficiency falls if the same size equipment is assumed; alternatively, larger equipment is needed to achieve the same removal efficiency. Any removal efficiency is theoretically possible if a suitable scrubber liquid exists, but achieving very high efficiencies (>99%) is much more costly than lower efficiencies.

If the absorber fluid is water (the most common fluid used in the organic chemical industry), the system can be designed to either treat and discharge the absorber liquid effluent or to strip the organic from the effluent and recycle the water. For non-aqueous fluids, stripping and recycle is normally the sole option. For water systems, the decision is based on economics—a stripping-recycle system is used when the cost of annual treatment for the organics in the effluent exceeds the annual cost for both the stripping system and the incrementally larger absorption system that is required. This breakpoint ranges approximately 1 to 5 mole %, based on the economic assumptions in this study. Generally speaking, waste gases containing less than 1 to 5 mole % of VOC and that are suitable for water absorption can be controlled more cost effectively with a "once-through, treat-and-discharge" absorption system. Of course, once-through systems may be applicable in industries where the absorber liquid can be fed to another process unit operation.

Absorption can be a VOC recovery technology if a stripper is provided or if the absorber liquid can be recycled to another process unit operation.

Condensation

The primary physical property affecting the use of condensers for VOC control is the vapor pressure of the VOC component at the condenser temperature. Condensation occurs in a condenser until the partial pressure of the VOC in the waste gas is just less than the vapor pressure at the condenser temperature. Any VOC can be removed to any given removal efficiency at a sufficiently low temperature. Since low-temperature coolants require refrigeration equipment, condensation at very low temperatures becomes impractical, even if technically feasible.

Condensation for air-pollution control is limited to control of waste gases with flowrates up to 2000 ft^3/min (3400 m^3/hr). This is related to the very large volume of non-condensable carrier gases which must sweep through the condenser.

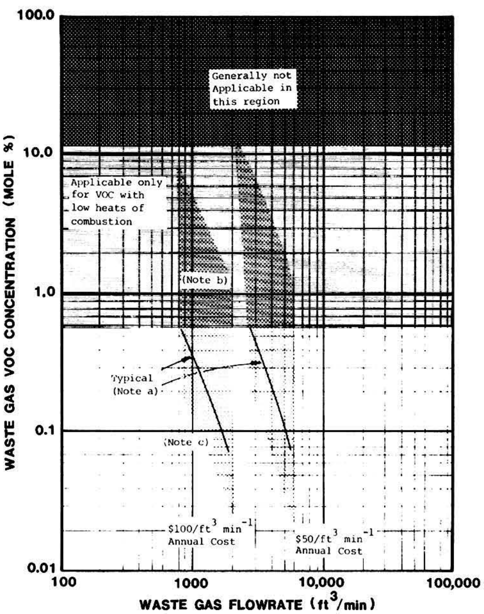
A major consideration in the use of a condenser is the problem associated with the freezing of the waste-gas components onto the condenser surface. Commonly, streams with high humidity require a warming cycle to periodically thaw the ice from the heat-exchange surface. Other VOC which solidify at condenser temperatures may require high maintenance or thermal cycling, or they may limit the removal efficiency of the more volatile VOC.

Generally speaking, VOC condensed with a refrigerated condenser is a candidate for chemical recovery and therefore may show extremely favorable economics. In fact, the present widespread use of condensers (refrigerated or not) to remove VOC from waste gases attests to the general applicability and economy of this device.

ECONOMIC AND ENERGY CONSIDERATIONS

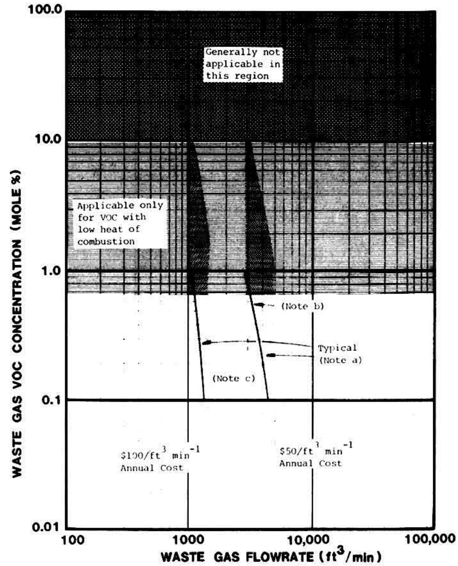
Summaries of the relative costs of the various control devices and diagrams of the regions of VOC concentrations and flowrates in which such a device is applicable are presented in Figures 2 through 13. Lines of constant annual cost are plotted over the applicable flow and concentration regions. The lines represent a typical emission defined for each technology. Shaded regions above or below the lines represent variations in the significant physical parameters relating the VOC concentration to the system design.

Normally, these costs represent worst-case costs, since the designs on which the costs were based are conservative. For instance, waste gases fed to thermal oxidizers are assumed not to contain any oxygen. Therefore, the flow of all combustion air required to burn the VOC is added and the combustion chamber and fuel requirements are greater than if a VOC-in-air waste gas is assumed. Costs for waste gases in air (containing sufficient oxygen so that no additional combustion air is needed) may be estimated by multiplying the waste-gas flowrate by 0.7 for catalytic oxidation, 0.5 for conventional thermal oxidation, and 0.2 for high-temperature thermal oxidation and using the costs associated with those flowrates. More exact methods are explained in the CDE reports.



NOTES: a. Typical case relates to an emission with VOC having a heat of combustion of 730,250 Btu/lb-mole.
b. VOC with heat of combustion less than 730,250 Btu/lb-mole.
c. VOC with heat of combustion greater than 730,250 Btu/lb-mole.
d. 730,250 Btu/lb-mole = 1,696,400 J/g-mole.

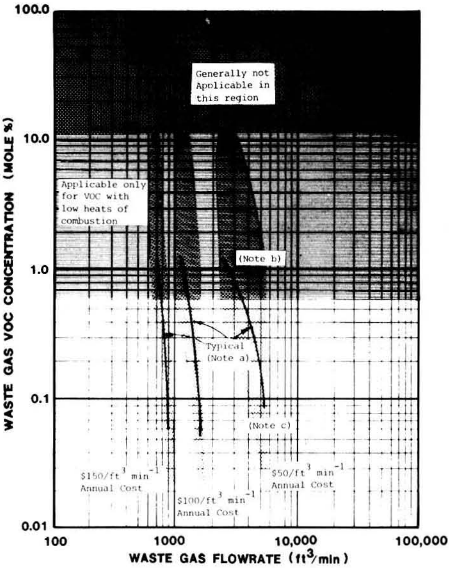
Figure 2. Application regime and annual costs for a catalytic oxidizer with no heat recovery (1200°F, 650°C)



NOTES: a. Typical case relates to an emission with VOC having a heat of combustion of 730,250 Btu/lb-mole.
b. VOC with heat of combustion less than 730,250 Btu/lb-mole.
c. VOC with heat of combustion greater than 730,250 BTU/lb-mole.
d. 730,250 Btu/lb-mole = 1,696,400 J/g-mole.

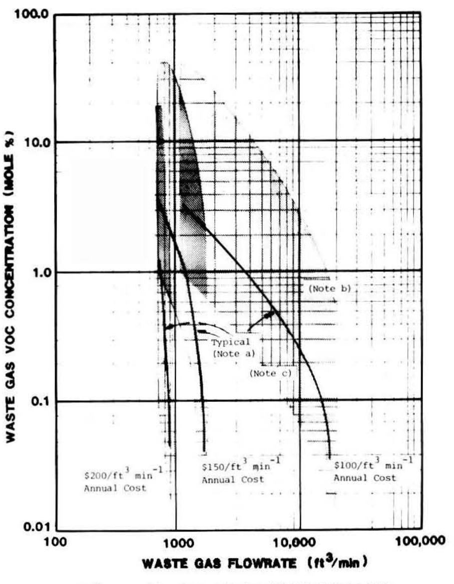
Figure 3. Application regime and annual costs for a catalytic oxidizer with recuperative heat recovery (1200°F, 650°C)

The absorption curve in Figure 13 is different from the others. This curve assumes that the absorption system uses a stripper with steam ratios of 0.1 and 0.2 moles of steam/ moles of waste gas and that 99% of the VOC is removed for all cases. Under these assumptions the cost of the absorp-



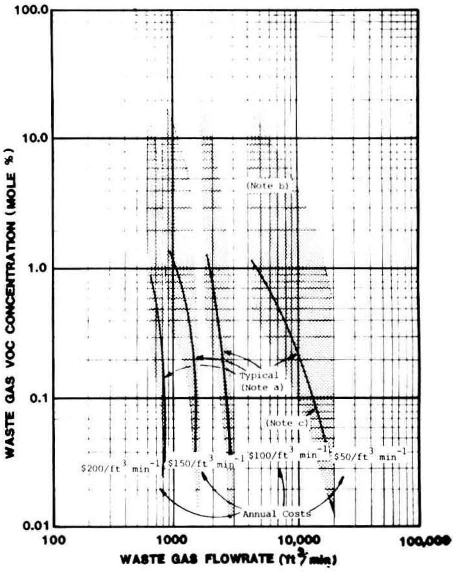
NOTES:
a. Typical case relates to an emission with VOC having a heat of combustion of 730,250 Btu/lb-mole.
b. VOC with heat of combustion less than 730,250 Btu/lb-mole.
c. VOC with heat of combustion greater than 730,250 Btu/lb-mole.
d. 730,250 Btu/lb-mole = 1,696,400 J/g-mole.

Figure 4. Application regime and annual costs for a catalytic oxidizer with a waste heat boiler (1200°F, 650°C)



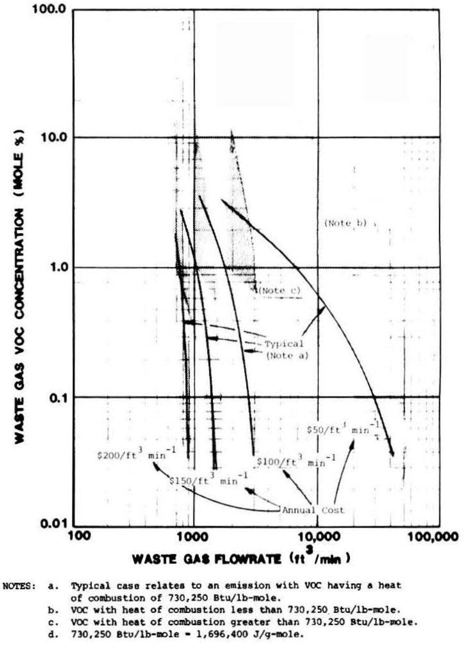
NOTES:
a. Typical case relates to an emission with VOC having a heat of combustion of 730,250 Btu/lb-mole.
b. VOC with heat of combustion less than 730,250 Btu/lb-mole.
c. VOC with heat of combustion greater than 730,250 Btu/lb-mole.
d. 730,250 Btu/lb-mole = 1,696,400 J/g-mole.

Figure 5. Application regime and annual costs for a conventional thermal oxidizer with no heat recovery (1600°F, 870°C)



NOTES:
a. Typical case relates to an emission with VOC having a heat of combustion of 730,250 Btu/lb-mole.
b. VOC with heat of combustion less than 730,250 Btu/lb-mole.
c. VOC with heat of combustion greater than 730,250 Btu/lb-mole.
d. 730,250 Btu/lb-mole = 1,696,400 J/g-mole.

Figure 6. Application regime and annual costs for a conventional thermal oxidizer with recuperative heat recovery (1600°F, 870°C)



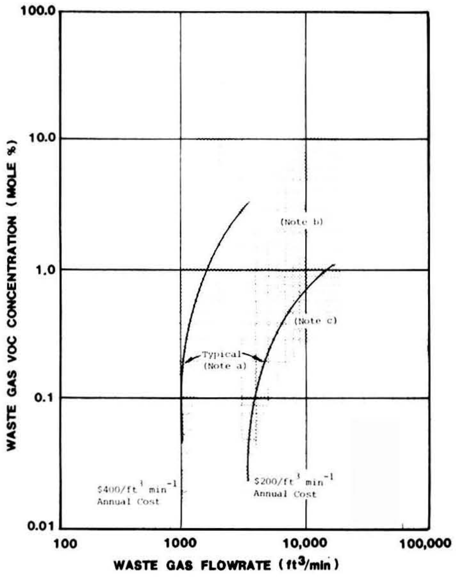
NOTES:
a. Typical case relates to an emission with VOC having a heat of combustion of 730,250 Btu/lb-mole.
b. VOC with heat of combustion less than 730,250 Btu/lb-mole.
c. VOC with heat of combustion greater than 730,250 Btu/lb-mole.
d. 730,250 Btu/lb-mole = 1,696,400 J/g-mole.

Figure 7. Application regime and annual costs for a conventional thermal oxidizer with a waste heat boiler (1600°F, 870°C)

tion system is independent of VOC concentration at less than 10 mole % (absorbers used for streams above this concentration are commonly process unit operations). The annual cost *versus* the slope of the gas-liquid equilibrium line for the VOC in the absorber liquid is shown in Figure 13.

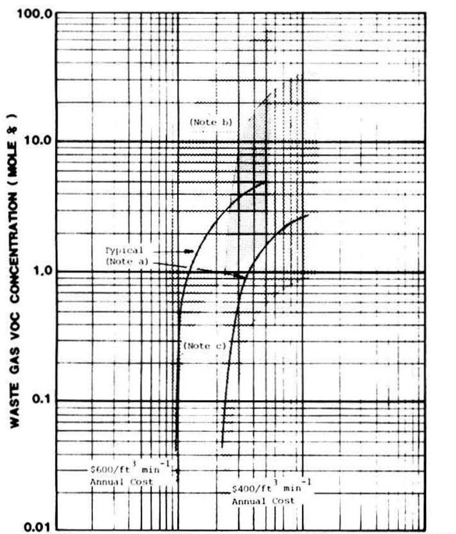
Costs of flares and the use of emissions as fuels are not included because their annual costs are not functions of VOC concentrations. (Annual costs for elevated flares typically range under $\$100/\text{ft}^3\text{min}^{-1}$ for flowrates between 300 to 50,000 ft^3 min or $\$59/\text{m}^3\ \text{hr}^{-1}$ between 510 to 85,000 m^3/hr).

Recovery credits for VOC were ignored in this presentation (although included in the CDE reports) and annual costs where recovery is possible may be small or savings may even occur. Technologies where VOC may be recovered are carbon adsorption, condensation, and absorption.



NOTES:
a. Typical case relates to an emission with VOC having a heat of combustion of 746,000 Btu/lb-mole.
b. VOC with heat of combustion less than 746,000 Btu/lb-mole.
c. VOC with heat of combustion greater than 746,000 Btu/lb-mole.
d. 746,000 Btu/lb-mole = 1,733,000 J/g-mole.

Figure 8. Application regime and annual costs for a high temperature thermal oxidizer with a waste heat boiler (2200°F, 1200°C)

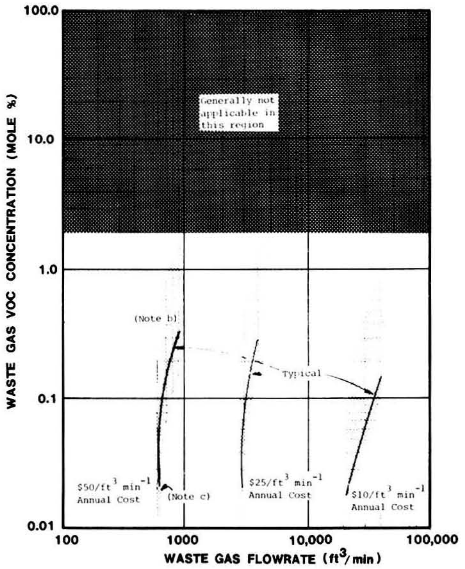


NOTES:
a. Typical case relates to an emission with VOC having a heat of combustion of 746,000 Btu/lb-mole.
b. VOC with heat of combustion less than 746,000 Btu/lb-mole.
c. VOC with heat of combustion greater than 746,000 Btu/lb-mole.
d. 746,000 Btu/lb-mole = 1,733,000 J/g-mole

Figure 9. Application regime and annual costs for a high temperature thermal oxidizer with a waste heat boiler (2600°F, 1430°C)

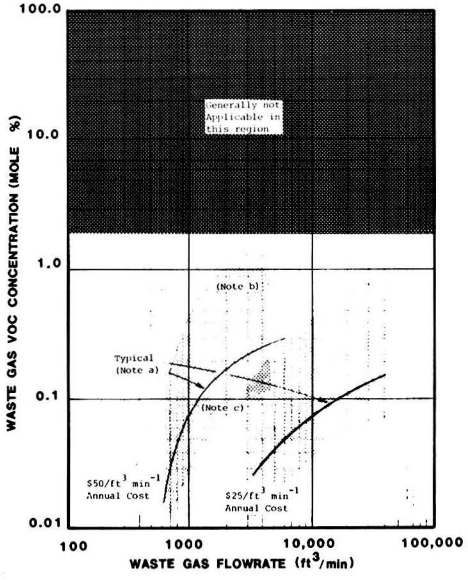
Where recovery has potential, these curves probably represent an extremely high cost limit.

These curves may be used to quickly estimate the annual cost of a control device for comparative purposes. The accuracy of this method is loose and CDE reports, vendors, and other references should be used before the final selection of a control technology is made.



NOTES:
a. Typical case is an emission with VOC having a molecular weight of 100 and an operating capacity of 7 g VOC/100 g carbon.
b. VOC molecular weight less than 100 and/or operating capacity greater than 7 g/100 g carbon.
c. VOC molecular weight greater than 100 and/or operating capacity less than 7 g/100 g carbon.

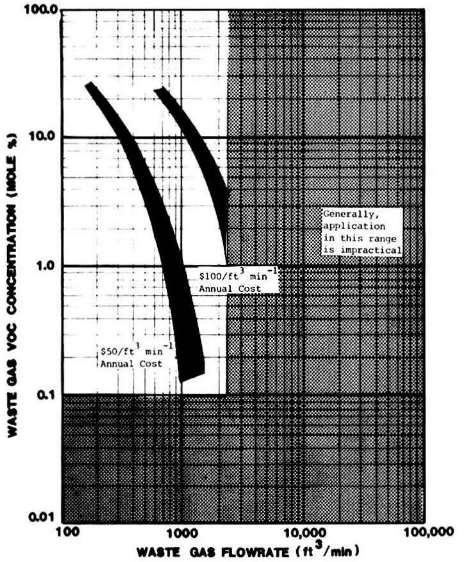
Figure 10. Application regime and annual costs for a carbon adsorber (Steam usage of 0.3 g of steam/g of carbon



Notes:
a. Typical case is an emission with VOC having a molecular weight of 100 and an operating capacity of 7 g VOC/100 g carbon.
b. VOC molecular weight less than 100 and/or operating capacity greater than 7 g/100 g carbon.
c. VOC molecular weight greater than 100 and/or operating capacity less than 7 g/100 g carbon.

Figure 11. Application regime and annual costs for a carbon adsorber (Steam usage of 2.0 g of steam/g of carbon

Different control devices have different VOC removal or destruction efficiencies and several technologies are limited only by economics as to the maximum VOC removal. A summary of the various technologies with the annual cost divided by the annual amount of VOC removed is presented in Table 3. This VOC-based cost effectiveness

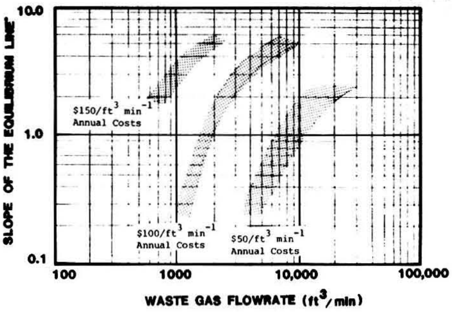


Application Regime and Costs for Refrigerated Condenses (VOC removal efficiency between 80 - 95%)

Figure 12. Application regime and annual costs for refrigerated condensers

differs from the flowrate-based cost effectiveness since removal or destruction efficiencies are factored in. These values are for illustration and comparative purposes only because VOC removal or destruction efficiencies are often a design variable and the values may have a significant excursion in cases where removal or destruction efficiencies are different from those assumed in the Table 3 cases.

The flow-based air energy effectiveness (Btu/ft³ of waste gas of kJ/m³ of waste gas) values are presented in Table 4. These values are essentially constant with flowrate. The ranges of energy consumption for the control of typical waste gases are shown.



*Gas-liquid equilibrium between the waste gas and the scrubber liquid (normally water).

Figure 13. Application regime and annual costs for absorbers with strippers

SUMMARY

A variety of control devices are presently in use for the control of volatile organic compounds (VOC) from potential organic air-pollution sources. Thermal oxidation, catalytic oxidation, flares, the use of emissions as fuels, carbon adsorption, absorption, and condensers are examples of these control devices. This paper has presented a brief description of the limitations of each of these technologies and has discussed the emission-flow and VOC-concentration range over which each one is applicable. The cost-effectiveness range (cost for each pound or kilogram of VOC destroyed or removed) and flow-based energy effectiveness range have also been presented. This paper should aid the environmental control engineer in preliminary selection of the best device or devices for a specific organic emission.

ACKNOWLEDGMENTS

I would like to acknowledge the contributions of the Emission Standards and Engineering Division of the U.S. EPA Office of Air Quality Planning and Standards (Re-

TABLE 3. REPRESENTATIVE COST-EFFECTIVENESS FOR ORGANIC EMISSION CONTROL TECHNOLOGY

Waste Gas Flow (ft³/min)	VOC Concentration[a]	Cost Effectiveness (per lb of VOC) for Condensation[b]	Absorption[c]	Adsorption[d]	Flares[e]	Catalytic Oxidation[f]	Thermal Oxidation[g]	High-Temperature Oxidation[h]
500-700	Low	\$0.20	i	i	j	\$0.31-0.37	\$0.55-0.62	\$0.78-1.29
	Medium	0.03	i	i	j	k	0.09-0.11	0.20-0.30
	High	0.06	i	i	i	k	0.06	0.12-0.17
1000	Low	0.14	\$0.56-1.07	\$0.13-0.15	j	i	i	i
	Medium	0.02	0.06-0.11	k	j	k	i	i
	High	0.04	i	k	\$0.001	k	i	i
5000	Low	l	0.20-0.55	0.06-0.08	j	0.09-0.12	0.25-0.29	0.44-0.78
	Medium	l	0.04-0.08	k	j	k	0.02-0.04	0.13-0.19
	High	l	i	k	i	k	0.01	0.09-0.12
50,000	Low	l	0.02-0.18	0.03-0.05	j	0.05-0.07	0.20-0.24	0.37
	Medium	l	0.10-0.45	k	j	k	0.01-0.02	0.11
	High	l	i	k	i	k	0.007	0.08

[a] Low ≅ 0.5 vol. % or 10 Btu/ft³; medium ≅ 5 vol. % or 50 Btu/ft³; high ≅ 20 vol. % or 100 Btu/ft³.

[b] 95% removal efficiency; no VOC credit.

[c] 99% removal efficiency; $L_m/mG_m = 1.4$; steam ratio = 0.2 moles of steam/mole of waste gas; no VOC credit.

[d] 70-12 ppm effluent; 6.96 lb of carbon/1000 ft ³; no VOC credit; loading-0.1 lb of VOC/lb of carbon, molecular weight of VOC = 50.

[e] Based on 100% VOC of propylene at 100% of capacity. Flares normally operate intermittently at a low fraction of capacity.

[f] 90-99% destruction efficiency; no heat recovery.

[g] 90-99% destruction efficiency; no heat recovery, 1400-1600°F (760-870°C) combustion temperature.

[h] 99.9% destruction efficiency; no heat recovery, 2200-2600°F (1200-1430°C) combustion temperature.

[i] Costs not available.

[j] Not applicable at low concentrations.

[k] Not applicable at high concentrations.

[l] Not applicable at high flow rates.

Conversion factors: \$/lb × 2.203 = \$/kg
Btu/ft³ × 37.24 = kJ/m³
lb/1000 ft³ × 16.03 = lb/1000 m³
lb/lb = g/g

TABLE 4. TYPICAL ENERGY EFFECTIVENESS OF ORGANIC EMISSION CONTROL DEVICES

Waste Gas VOC Concentration (mole%)	Energy Effectiveness (Btu consumed/ft³ of waste gas controlled)									
	Thermal Oxidation with No Heat Recovery[a]			Thermal Oxidation with Waste Heat Boiler[a]						
	Catalytic (1200°F)	Conventional (1600°F)	High Temperature (2600°F)	Catalytic (1200°F)	Conventional (1600°F)	High Temperature (2600°F)	Flare with Smokeless Combustion[a]	Carbon Adsorber[a]	Refrigerated Condenser[b]	Absorber with Stripping[a,c]
0.1	40	83	330	27	31	100	d	2-12	0.1-0.2	5-10
1.0	d	62	300	d	10	70	d	4-24	0.5-1.0	5-10
10.0	d	d	70	d	d	−160[e]	0.02	d	2-4	5-10

[a] Energy primarily thermal, electrical consumption low.
[b] Energy primarily electrical, thermal consumption low.
[c] Based on systems using steam stripping of the absorber fluid. Once-through systems consume much less energy.
[d] Generally not applicable in this concentration range.
[e] Energy produced.
Conversion factors: Btu/ft³ × 37.24 = kJ/m³
(°F + 460)/1.8 − 273 = °C

search Triangle Park, North Carolina) without whose help and support this work would not have been possible. I would like to thank the other authors of the control device evaluation reports prepared for the EPA, H. S. Basdekis, J. A. Key, V. Kalcevic, C. S. Parmele, D. G. Erikson, and R. L. Standifer, for their assistance and insight leading to this summary paper. Finally, I would like to thank my wife, Christine, for her help in organizing and analyzing the data in this study.

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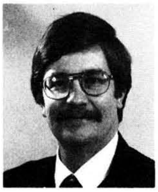

J. W. Blackburn is presenty a senior project engineer in the Research and Development Group of IT Enviroscience. There he is responsible for engineering and ventures analysis activities. He has had 10 years of experience in the application of chemical engineering technologies to air pollution, water pollution, solid waste problems and has published several papers in this area. He earned his B. S. ChE degree in 1973 from the University of Cincinnati, is a member of the AIChE and is a registered professional engineer in the State of Ohio.

Mass Transfer in Ozone Absorption

An approximate analytical equation is derived for predicting the enhancement of mass transfer by decomposition and ozanation reactions.

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The mass transport of ozone into aqueous solutions is important in both air and water pollution abatement. Absorption and reactions of ozone with organic and inorganic compounds in liquid drops has been suspected to play a major role in the formation and accumulation of secondary aerosols in the atmosphere [*24*]. On the other hand, ozone has been used for the disinfection of drinking water and treatment of industrial waste waters for many years [29] because of its high oxidation potential. All these applications involve reactions of ozone in the gas phase with one or more constituents in the liquid phase. But before ozone can react with any substance in the liquid phase, whether the liquid is water or an organic solvent, it must pass through an inter-

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face between the two phases. This transfer of ozone from one phase to another is via diffusion and convective mass transport [*30*].

The mechanism of the gas-liquid reaction system can be visualized as consisting of several steps. These include diffusion of ozone through the gas phase into an interface between the gas and liquid phases, transport across the interface to the liquid-phase boundary, and transfer into the bulk liquid. The dissolved ozone may be depleted in each of these steps by decomposition or reactions with reactants diffusing from the liquid phase. Products formed in the reactions may penetrate across the phase boundary into the main liquid or may diffuse back into the gas phase if they are volatile.

In this paper, the relative importance of diffusion in each step is examined and fundamental concepts governing transport of a gas into the liquid phase are introduced. Effects of decomposition and ozonation reactions on the rate of mass transfer of ozone are investigated. On the basis of the film theory, a mathematical model taking into account molecular diffusion and simultaneous decomposition and ozonation reactions has been developed to predict enhancement of mass transfer by the chemical reactions. Methods for estimation of chemical mass-transfer coefficients for ozone absorption processes in gas-liquid contactors are discussed and illustrated.

MASS TRANSFER BETWEEN PHASES

The transport of a solute from one phase to another is a result of a concentration gradient, as sketched in Figure 1. In the absorption of a gas by a liquid, it can be assumed that a fairly uniform composition is maintained in the bulk gas because of turbulent motion. As suggested by the two-film concept of Lewis [*18*] and Whitman [*36*], the solute A must diffuse through a laminar layer between the gas bulk and the interface and another layer between the interface and the liquid bulk. Once the solute approaches the liquid-phase boundary, it is carried away by eddy diffusion into the turbulent liquid which is well mixed at a constant concentration. At steady state, the rate of diffusion of the solute A from the gas to the interface is equal to the rate from the interface to the bulk liquid

$$N_A = k_G'(p_{Ag} - p_{Ai}) = k_L'(C_{Ai} - C_{AL}) \qquad (1)$$

In the above equation, the individual mass-transfer coefficients are denoted by k_G' and k_L', respectively, for gas and liquid films. The mass-transfer flux also can be expressed in terms of the overall mass-transfer coefficients, K_G' and K_L', as follows:

$$N_A = K_G'\,(p_{Ag} - p_{AL}) = K_L'\,(C_{Ag} - C_{AL}) \qquad (2)$$

Steady-State Equations

The steady-state equations describe a dynamic equilibrium which is established by the common substance between the two insoluble phases. For example, if an air-ozone gas mixture is brought into contact with distilled water, the ozone will be absorbed into the water until the water becomes saturated. At a fixed temperature, the partial pressure of A is a linear function of the mole fraction of A in a dilute solution in accordance with Henry's law:

$$p_A = H\,x_A = HC_A/C \qquad (3)$$

where the total concentration, C, is about 0.056 mole/cm^3 for dilute solutions. If the two phases can be assumed in equilibrium at the interface, then Equations (1), (2) and (3) can be combined to yield the following relationships between the overall and individual mass-transfer coefficients:

$$\frac{1}{K_G'} = \frac{1}{k_G'} + \frac{H}{Ck_L'} \qquad (4)$$

and

$$\frac{1}{K_L'} = \frac{1}{k_L'} + \frac{C}{Hk_G'} \qquad (5)$$

The above equations suggest that the overall resistance to mass transfer is the sum of the individual resistances presented by the terms on the right-hand side.

Solubilities of ozone in water [*28,35*] and Henry's law constants [*27*] at various temperatures are illustrated in Figure 2. Since ozone is only slightly soluble in aqueous solutions, the Henry's law constant, H, is large, as indicated in the figure. Under this condition, the resistance in the gas film is negligible compared with that in the liquid film, and the mass-transfer process is controlled by the diffusion in the liquid film as can be seen from the above equations [*7,30*].

MASS TRANSFER MODELS

Many theories or models have been proposed to explain the phenomenon of mass transport in the region adjacent to the liquid-phase boundary. The most notable are the film, penetration, and surface-renewal theories. These models all postulate that the transport of mass in the region is predominantly by molecular diffusion in accordance with Fick's law and that convective transport is unimportant. Thus, the equation of continuity for unsteady-state, one-dimensional transport of the solute A can be written as

$$D_A \frac{\partial^2 C_A}{\partial z^2} = \frac{\partial C_A}{\partial t} \qquad (6)$$

where the diffusion coefficient or molecular diffusivity of A into the liquid, D_A, is assumed independent of the concentration, C_A. At the interface (z = 0), the solute is in equilib-

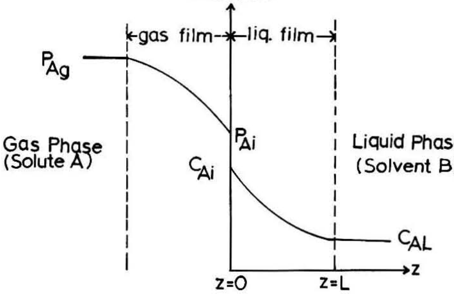

Figure 1. Mass transfer between phases.

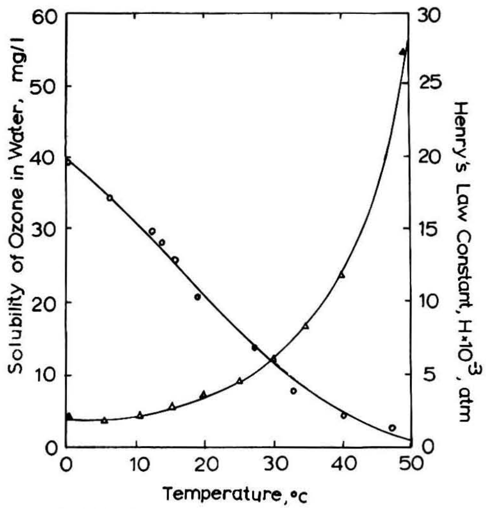

Figure 2. Solubility of ozone in water and Henry's law constant.

rium with the liquid elements or film at the concentration, C_{Ai}. At the outer edge of the film or an element ($z = L$), the concentration of the solute, C_{AL}, is identical to that in the bulk liquid, which is well mixed. Thus, the differential equation (6) with the associated conditions can be solved to obtain the concentration profile of A in the liquid film or an element. The instantaneous rate of absorption of A per unit surface area, then, can be derived from

$$N_A(t) = -D_A\left(\frac{\partial C_A}{\partial z}\right)_{z=0} \qquad (7)$$

The theories differ in two main aspects in postulating the theoretical mechanism for interphase mass transport. One aspect deals with diffusional behavior of the transporting species, and the other with hydrodynamic activities of the two phases near the interface.

As mentioned earlier, the film theory of Lewis [*18*] and Whitman [*36*] is based on the assumption that when two fluid phases are brought in contact with each other, there exists on each side of the phase boundary a thin layer of stagnant fluid. The liquid film is considered very thin, without any accumulation of the diffusing mass. Thus, steady-state diffusion prevails and the concentration distribution is a linear function of the distance in the liquid film, as can be seen from Equation (6). The average rate of mass transfer is identical to the point rate of mass transfer for the film theory, and can be derived from Equation (7) as,

$$\bar{N}_A = N_A = D_A(C_{Ai} - C_{AL})/L \qquad (8)$$

By defining the liquid-side mass-transfer coefficient k_L', in terms of the concentration driving force, $(C_{Ai} - C_{AL})$,

$$\bar{N}_A = k_L'(C_{Ai} - C_{AL}) \qquad (9)$$

then the expression for k_L' can be derived for the film theory as

$$k_L' = D_A / L \qquad (10)$$

Penetration Theory

The penetration theory postulated by Higbie [*10*] assumes that turbulent eddies travel from the bulk of the phase to the interface, where they remain for a short time. If the exposure time is short, it is possible that a steady-state concentration gradient within a film may never have been achieved before the film is disrupted or replaced. Also, the transporting species may never approach the outer edge of the liquid film or element in the short contact time, and the thickness of the liquid film or element may be assumed infinite. The partial differential equation (6) governing unsteady-state diffusion of the transporting species is applicable according to the penetration concept, and the instantaneous rate of mass transfer for an individual surface element can be derived from Equation (7). Higbie [*10*] assumed that every surface element is exposed to the solute for the same length of time, t_o, before being replaced. Therefore, the average mass flux can be derived to be

$$\bar{N}_A = \frac{1}{t_o}\int_o^{t_o} N_A(t)dt = 2(C_{Ai} - C_{AL})\sqrt{D_A / (\pi t_o)} \qquad (11)$$

The expression for the liquid-side mass-transfer coefficient is obtained from equations (9) and (11) as

$$k_L' = 2\sqrt{D_A / (\pi t_o)} \qquad (12)$$

Instead of a constant time of exposure, the surface-renewal theory of Danckwerts [*6*] pictures the liquid phase as completely disturbed by numerous infinitesimally small phase elements or eddies in the phase. These eddies are constantly changing the structure and position resulting in turbulence in the interface boundary. Dackwerts proposed that the eddies may vary at locations but are continuously bringing microscopic masses of fresh phase from the bulk to the interphase surface. The chance of an element or eddy being replaced with fresh liquid is assumed independent of the length of time of exposure. If the fraction of the surface is replaced at a rate s, Danckwerts [*6*] showed that the distribution of the surface age can be represented by

$$\phi(t) = se^{-st} \qquad (13)$$

Danckwerts Theory

The Danckwerts surface-renewal theory adopts this surface-renewal concept to represent the hydrodynamic behavior and the unsteady-state molecular diffusion for the transport activities through the elements or eddies. Thus, the concentration distribution and point mass-transfer rate can be derived from Equations (6) and (7), respectively. The average rate of mass transfer per unit area is

$$\bar{N}_A = \int_o^\infty N_A(t)\, s\, e^{-st}dt = \sqrt{D_A s}\,(C_{Ai} - C_{AL}) \qquad (14)$$

The expression for the liquid-side mass-transfer coefficient is

$$k_L' = \sqrt{D_A s} \qquad (15)$$

In addition to the above theories, other models also have been proposed in the literature [*7*] to describe the diffusional behavior or hydrodynamic conditions at the interface. For example, Dobbins [*8*] and Toor and Marchello [*32*] suggested in a film-penetration model that the equilibrium condition may be established in a surface element of finite thickness after a long residence time. They showed that the film and the penetration theories are not separate concepts but merely limiting cases of the more general film-penetration model. Rate equations derived by these authors indicated the dependence of the mass-transfer coefficient on the diffusivity in the following form:

$$k_L' \propto D_A^{\nu} \qquad (16)$$

where ν may vary from 0.5 to 1.0, as concluded by many experimental investigations [*30*]. According to the penetration and surface-renewal concepts, ν is equal to 0.5, while, on the other hand, the film theory yields unity for ν. It should be noted that the rate equations derived from various theories contain at least one parameter which is not, in general, experimentally measurable. Therefore, quantitative verification of the various theories may not be permissible.

Enhancement of Mass Transfer by Ozonation

The resistance to the transport of ozone from a gas phase into the interface is insignificant, as discussed earlier. The process of ozone absorption by a liquid, therefore, is controlled mainly by molecular diffusion of the dissolved ozone and chemical reactions in the region between the interface and the liquid-phase boundary. In this region, laminar flow behavior prevails and eddy diffusion is unimportant. Once the ozone approaches the phase boundary, it is carried away into the turbulent liquid by eddy diffusion. Since the eddy diffusivity is much greater than the molecular diffusivity, the liquid bulk provides little resistance to the overall mass transfer.

As the ozone diffuses toward the liquid-phase boundary, it may decompose to oxygen. Simultaneously, the ozone also may react with a contaminant penetrating from the bulk liquid. The parallel reactions may be expressed in the following form:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{P}_s$$

$$\mathrm{A} + b\mathrm{B} \xrightarrow{k_2} Q_s$$

and the rates of depletion of the ozone (A) and the liquid reactant (B) by the reactions are

$$R_A = -k_1\, C_A^{l} - k_2\, C_A^{m} C_B^{n} \qquad (17)$$

and

$$R_B = -\, k_2\, C_A^{m} C_B^{n} \qquad (18)$$

The one-dimensional, unsteady-state diffusion accompanied by the decomposition and ozonation reactions within the liquid film or element are, therefore, governed by the following set of partial differential equations:

$$D_A\frac{\partial^2 C_A}{\partial z^2} + R_A = \frac{\partial C_A}{\partial t} \qquad (19)$$

$$D_B\frac{\partial^2 C_B}{\partial z^2} + bR_b = \frac{\partial C_B}{\partial t} \qquad (20)$$

For many ozonation systems commonly encountered in practice [*19,31*], the decomposition reaction can be considered first order ($\ell = 1$), and the ozonation reaction second order (with first order in both concentrations of the ozone and the constituent in the liquid, $m = n = 1$). Also, the effect of unsteady-state transfer on enhancement of mass transfer by chemical reactions can be ignored [*15*]. By combining Equations (17) to (20) inclusive, the equations of continuity for the steady-state diffusion and parallel reactions can be rewritten as,

$$D_A\frac{d^2 C_A}{dz^2} - k_1 C_A - k_2 C_A C_B = 0 \qquad (21)$$

$$D_B\frac{d^2 C_B}{dz^2} - bk_2 C_A C_B = 0 \qquad (22)$$

Approximate Approach

The above mathematical system is nonlinear and an exact solution has not been possible. In the present work, therefore, an approximate approach will be employed to study the enhancement of mass transfer by the chemical reactions. As the liquid constituent B diffuses from the bulk liquid into the interface, it reacts with the dissolved ozone and the concentration C_B declines along the path of diffusion. At the interface, the chemical species B is maintained at a low concentration C_{Bi} or is completely depleted if the ozonation reaction is fairly fast. Similar to the approach used by Van Krevelen and Hoftijer [*33*] for a simpler system, therefore, an approximate profile for the concentration of B is employed by assuming a constant concentration, C_{Bi}, for B within the liquid film. The concentration changes stepwise to C_{BL} at the outer edge of the liquid film and is maintained at C_{BL} in the main liquid, which is well mixed. By this linearization, an analytical solution to Equation (21) can be derived, and an expression for the mass flux of A can be obtained from Equation (7). A relationship between the mass flux $\bar{N}_A$, and the interfacial concentration, C_{Bi}, also can be derived from Equations (21) and (22).

For a system of diffusion accompanied by chemical reactions, the chemical mass-transfer coefficient, k_L, can be defined in terms of the concentration driving force, $(C_{Ai} - C_{AL})$,

$$\bar{N}_A = k_L\,(C_{Ai} - C_{AL}) \qquad (23)$$

The concentration of A at the outer edge of the film, C_{AL}, may be taken as zero by considering complete depletion of the dissolved ozone in the film if the liquid constituent, B, is relatively reactive with A.

The influence of chemical reactions on the absorption rate can be investigated in terms of the enhancement factor, E, which is defined by

$$E = k_L/k_L' \qquad (24)$$

Enhancement Factor

The expression for the enhancement factor is derived for the system described above as,

$$E = M^{1/2}/\tanh M^{1/2} \qquad (25)$$

where

$$M = M_1 + M_2\,[1-(E-1)/Q] \qquad (26)$$

$$Q = (D_B/D_A)\,(C_{BL}/C_{Ai})\,/b \qquad (27)$$

$$M_1 = k_1 D_A/k_L'^2 \qquad (28)$$

and

$$M_2 = k_2\, C_{BL}\, D_A/k_L'^2 \qquad (29)$$

As can be seen from the above equations, the enhancement factor, E, is a function of the three dimensionless parameters, Q, M_1, and M_2. The enhancement factor can be calculated by iteration for a given set of the parameters, and is presented graphically in Figures 3, 4, 5, and 6.

The analytical approximate equation is applicable to ozone absorption processes involving a first-order decomposition reaction and a second-order ozonation reaction. Although various orders of decomposition of ozone in aqueous

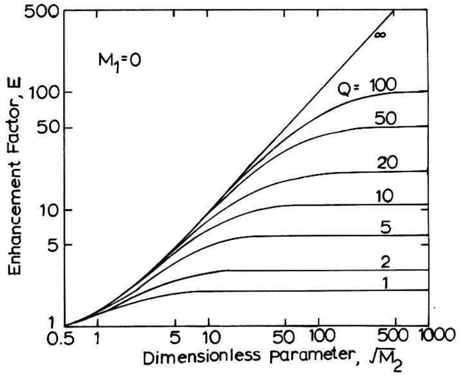

Figure 3. Enhancement factor for ozone absorption processes ($M_1 = 0$).

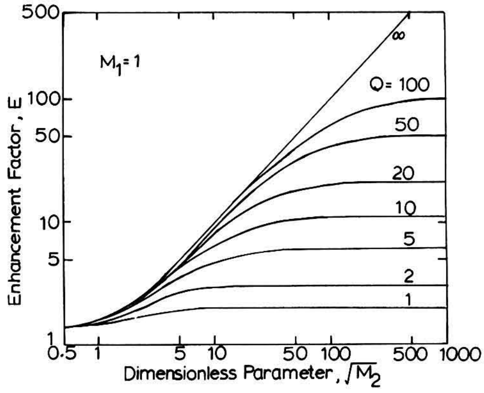

Figure 4. Enhancement factor for ozone absorption processes ($M_1 = 1$).

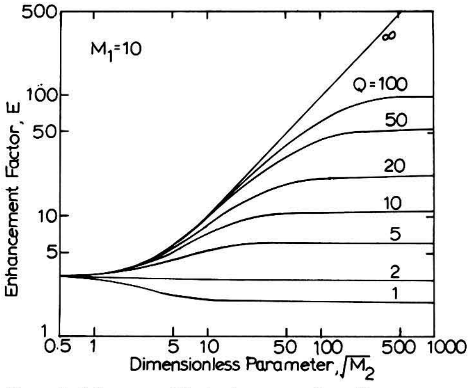

Figure 5. Enhancement factor for ozone absorption processes ($M_1 = 10$).

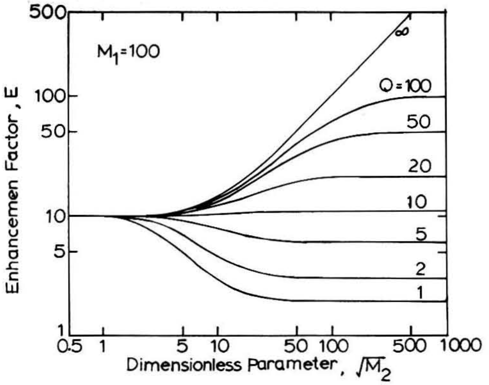

Figure 6. Enhancement factor for ozone absorption processes (M_I = 100).

solutions have been reported [2,9,17], the decomposition reaction often can be approximated by first-order kinetics [31]. Kinetic data for ozonation reactions between ozone and organic compounds have been correlated frequently by second-order kinetics [13,14,19,21]. For ozone absorption accompanied by parallel reactions of different orders, numerical methods can be employed to predict the enhancement factor [16,20,22,25]. Comparisons of results predicted by both the analytical approximations and numerical techniques were made by Mehta [22]. He showed that the analytical approximate equation developed in this work yields a maximum error of 15% in the prediction of the enhancement factor. For simpler systems of mass transfer with a single-step reaction, Peaceman [26] reported that the analytical approximation is correct within 10% in the theoretical predictions of the enhancement factor.

CHEMICAL MASS TRANSFER COEFFICIENTS

The chemical mass-transfer coefficient, k_L, for a system of molecular diffusion accompanied by decomposition and ozonation reactions can be evaluated from a knowledge of the physical mass-transfer coefficient and the effects of the chemical reactions on mass transfer. By utilizing the relationship given in Equation (24), one can write

$$k_L = k_L' E \tag{30}$$

In the above equation, k_L' represents the liquid side, physical mass-transfer coefficient for a corresponding ozone-absorption process without considering the effects of the chemical reactions. The enhancement factor, E, can be predicted from the theoretical approach discussed in the previous section.

Expressions for the physical mass-transfer coefficient have been derived on the basis of various theories, as discussed in an earlier section. Because of unknown parameters in these expressions, however, determination of the physical mass-transfer coefficient from the theoretical equations, in general, is not permissible. For practical applications, therefore, semi-empirical approaches are employed to obtain the physical mass-transfer coefficients.

Dimensional analyses indicate that the liquid-side mass-transfer coefficient can be correlated in terms of the Sherwood *(Sh)*, Schmidt *(Sc)*, and Reynolds *(Re)* numbers. For the rise of swarms of gas bubbles in bubble columns, Hughmark [11,12] showed that the following correlation is applicable with an average deviation of 15%:

$$\frac{k_L' d}{D_A} = Sh = 2 + 0.0187 \left[Re^{0.484}\, Sc^{0.339} \left(dg^{0.333}/D_A^{-0.667}\right)^{0.072}\right]^{1.61} \tag{31}$$

Correlations of the product of mass-transfer coefficient and specific interfacial area per unit volume of solution, $k_L' a$, have been made by Akita and Yoshida [1], Nakanoh and Yoshida [23] and others [27,30].

Methods for measurement and correlation of mass-transfer coefficients for the dispersion of gas in agitated vessels were reviewed by Van't Reit [34]. He reported that the $k_L' a$ value can be correlated in terms of power per unit volume and superficial gas velocity for separate systems with and without ions in solutions. For swarms of small bubbles with diameters less than 0.2 cm in mechanically stirred vessels, Calderbank [4,5] showed that the mass-transfer coefficient is independent of the Reynolds number.

$$k_L' = 20.89\, D_A^{0.67} \tag{32}$$

For large bubbles in agitated vessels, Calderbank [5] found that the mass-transfer coefficient can be correlated by

$$k_L' = 724.7\, D_A^{0.86} \tag{33}$$

Since the molecular diffusivity of ozone in dilute solutions, D_A, is about 2×10^{-5} cm²/s at room temperature, the above equations indicate that the physical mass-transfer coefficient increases from 0.015 cm/s for small bubbles to 0.066 cm/s for large bubbles in an agitated vessel. Correlations of mass-transfer coefficients for other gas-liquid contactors also are available in the literature [27,30,37]. Variables involved in design of liquid reactors have been reviewed by Barona and Prengle [3], and others.

The enhancement factor can be obtained from Equation (25) or Figures 3 to 6, as discussed in the previous section. In addition to the physical mass-transfer coefficient and molecular diffusivities, kinetic information is required to predict the enhancement factor.

The dispersion of small bubbles of an ozone-air mixture in wastewater containing cyclohexene in an agitated tank is used here as an example to illustrate the calculation procedures. The kinetics of ozonation of cyclohexene was studied recently by Keady and Kuo [13,14]. The reaction is second order and the reaction-rate constant, k_2, is about 3×10^6 liter/mole-s at room temperature. Furthermore, the rate constant was found to change very little with the pH value of the solution, and the stoichiometric ratio was determined to be unity. The rate of decomposition of ozone in aqueous solutions has been investigated by many researchers [2,9,17]. Assuming that the wastewater is neutral and contains cyclohexene at 100 ppm by weight, then, the first-order rate constant for the decomposition reaction can be estimated [31] to be about 0.001 s^{-1} at room temperature. The initial concentration of cyclohexene in the solution, C_{BL}, is calculated to be $1.217 \times 10^{-3}M$, and the solubility of ozone in the solution [28], C_{Ai}, is about $2.12 \times 10^{-4}M$. The diffusivity ratio, D_B/D_A, is assumed unity in this estimation. By utilizing Equations (27), (28), and (29), the following parameters are computed:

$$Q = (D_B/D_A)(C_{BL}/C_{Ai})/b = (1)(1.217 \times 10^{-3}/2.12 \times 10^{-4})/(1) = 5.74$$

$$M_I = k_I D_A/k_L'^2 = (0.001)(2 \times 10^{-5})/(0.015)^2 = 8.89 \times 10^{-5}$$

and

$$M_2 = k_2\, C_{BL}\, D_A/k_L'^2 = (3 \times 10^6)(1.217 \times 10^{-3})(2 \times 10^{-5})/(0.015)^2 = 324.5$$

Using the above values, the enhancement factor can be estimated from Equation (25) or Figure 3 to be about 6.5. From Equation (30), the chemical mass-transfer coefficient is

$$k_L = k_L' E = (0.015)(6.5) = 0.0975 \text{ cm/sec.}$$

As illustrated in the above example and noted earlier, the enhancement factor approaches $(1 + Q)$ for a very rapid ozonation reaction with a large M_2 value. Under this circumstance, the procedures for calculation of the enhancement factor can be greatly simplified.

Once the chemical mass-transfer coefficient is available, the rate of absorption of ozone in the solution can be computed. The absorption rate is proportional to the chemical mass-transfer coefficient, k_L, the concentration driving force, C_{Ai}, as well as the specific interfacial area per unit volume of solution, a. Therefore, it is advantageous in choosing a gas-liquid contractor such as an agitated vessel to provide a large interfacial area to the transport of absorbed ozone [*16*,*30*]. Also, it should be noted that the chemical mass-transfer rate and coefficients have been measured experimentally for several ozone-absorption systems as reported in the literature [*16*,*21*,*38*].

CONCLUSIONS

A mathematical model has been formulated for the absorption of ozone accompanied by a first-order decomposition of ozone and the second-order, ozonation reaction between ozone and a liquid reactant in gas-liquid contactors. On the basis of the film model, an analytical approximate equation has been derived to predict the enhancement of mass transfer by the decomposition and ozonation reactions. Methods for estimation of chemical mass-transfer coefficients for ozone-absorption processes have been suggested. By combining a knowledge of physical mass-transfer coefficients from empirical correlations and enhancement factors from theoretical predictions, the chemical mass-transfer coefficient for an ozone-absorption process can be estimated as illustrated in this paper.

ACKNOWLEDGEMENT

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NOTATION

a = Specific interfacial area, cm^2/cm^3 solution
b = Stoichiometric ratio of ozonation reaction
C_A = Concentration of component A(ozone), $mole/cm^3$
C_{Ag} = Concentration of component A in gas phase, $mole/cm^3$
C_{Ai} = Concentration of component A at the interface, $mole/cm^3$
C_{AL} = Concentration of component A in the bulk liquid, $mole/cm^3$
C_B = Concentration of component B(liquid reactant), $mole/cm^3$
C_{Bi} = Concentration of component B at the interface, $mole/cm^3$
C_{BL} = Concentration of component B in the bulk liquid, $mole/cm^3$
d = Bubble diameter, cm
D_A = Molecular diffusivity of A, cm^2/sec
D_B = Molecular diffusivity of B, cm^2/sec
E = Enhancement factor, $E = k_L/k'_L$
g = Gravitational acceleration, cm/sec^2
H = Henry's law constant, atm
k_1 = First-order rate constant for ozone decomposition, sec^{-1}
k_2 = Second-order rate constant for ozonation reaction, liter/mole-sec
k'_G = Gas-side mass transfer coefficient for physical absorption, $mole/cm^2$ sec atm
K'_G = Overall gas-phase mass-transfer coefficient, $mole/cm^2$ sec atm
k_L = Liquid-side mass-transfer coefficient for chemical absorption, cm/sec
k'_L = Liquid-side mass-transfer coefficient for physical absorption, cm/sec
K'_L = Overall liquid-phase mass-transfer coefficient, cm/sec
ℓ = Order of decomposition reaction of ozone
L = Thickness of a film or surface element, cm
m = Order of ozonation reaction with respect to ozone
M = Dimensionless parameter defined by Equation (26)
M_1 = Dimensionless parameter defined by Equation (28)
M_2 = Dimensionless parameter defined by Equation (29)
n = Order of ozonation reaction with respect to the liquid reactant
N_A = Point rate of mass transfer of A per unit interfacial area, $mole/cm^2$ sec
$\bar{N}_A$ = Average rate of mass transfer of A per unit interfacial area, $mole/cm^2$ sec
P_A = Partial pressure of component A, atm
P_{Ag} = Partial pressure of component A in gas phase, atm
P_{Ai} = Partial pressure of component A at the interface, atm
P_{AL} = Partial pressure of component A which is in equilibrium with the bulk liquid, atm
Q = Dimensionless parameter defined by Equation (27)
R_A = Rate of depletion of ozone by decomposition and ozonation reactions, $mole/cm^3$ sec
R_B = Rate of depletion of liquid reactant by ozonation reaction, $mole/cm^3$ sec
Re = Reynolds number, $Re = du\rho/\mu$
s = Fractional rate of surface renewal, sec^{-1}
Sc = Schmidt numbers, $Sc = \mu/(\rho D_A)$
Sh = Sherwood number, $Sh = k'_L d/D_A$
t = Time of diffusion, sec
t_o = Contact time at the interface, sec
u = Slip velocity of gas bubbles, cm/sec
x_A = Mole fraction of A
x_B = Mole fraction of B
z = Distance of diffusion, cm

Greek Letters

ρ = Density, g/cm^3
μ = Viscosity, g/cm sec
$\phi(t)$ = Surface age-distribution function
ν = Exponent power

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The Overland-Flow Process

A viable alternative for the removal of organic material from wastewaters? A predictive model.

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DEVELOPMENT OF A PREDICTIVE MODEL TO DESCRIBE THE REMOVAL OF ORGANIC MATERIAL WITH THE OVERLAND FLOW PROCESS

BACKGROUND

The overland-flow wastewater treatment process involves the application of wastewater to the top portion of carefully-graded, grass-covered slopes where various physical, biological, and chemical processes renovate the wastewater as it flows down the slope. Treated effluent from the process is collected in channels at the bottom of the slope. A schematic of the overland-flow process is shown in Figure 1. The overland-flow process has been demonstrated to be a viable method for the treatment of a wide variety of wastewaters ranging from high-strength food processing and agricultural wastewater to secondary treated municipal wastewater. When used for the treatment of raw or primary treated municipal wastewater, overland flow has been shown to be capable of producing effluents equal or superior in quality to those produced by conventional secondary treatment processes at a substantially lower cost [*1*] [2]. The Environmental Protection Agency (EPA) has recognized and encouraged the use of the overland-flow process as a viable alternative for municipal wastewater treatment when site conditions are suitable for its use [3]. Yet, implementation of the overland-flow process for municipal wastewater treatment has been very limited.

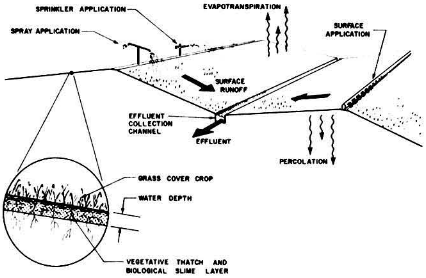

Figure 1. Overland-flow process schematic.

What is needed to advance overland-flow technology is a clear definition of the design and operating parameters and environmental factors that govern overland-flow process performance and an understanding of the relationship between these parameters and process performance. Such knowledge is necessary to develop functional relationships in the form of predictive models that can be used to predict reliably the effects of the governing design and operating parameters on process performance. Such predictive models would serve as a rational basis for the design and operation of overland-flow systems and would allow system design to be optimized to produce an effluent of specified quality at a minimum cost.

In an effort to meet these needs, the Department of Civil Engineering at the University of California, Davis, has undertaken an overland-flow research and demonstration project under the sponsorship of the California State Water Resources Control Board. The project is being conducted in two phases. Phase I involves pilot studies conducted indoors under semi-controlled environmental conditions. Phase II is a full-scale, 4.5-hectare (11-acre) field demonstration of the overland-flow process for the treatment of raw and primary treated municipal wastewater. The purpose of this paper is to present and discuss the results of the pilot studies and to present the formulation of a predictive model that can be used to describe the removal of wastewater constituents as a function of process design and operating parameters.

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Objectives

The overall objectives of the project are to formulate and verify a predictive model that can be used as a rational basis for the design and operation of overland flow systems and to demonstrate the capabilities of overland flow as a treatment process for raw and primary treated municipal wastewaters.

The specific objectives of this study include:

1) Establishment and definition of overland-flow design and operating parameters and units for their expression.
2) Construction of experimental facilities for the conduct of overland-flow pilot studies.
3) Development of pilot study procedures and conduct of studies to determine the effect of defined parameters on overland-flow treatment performance.
4) Formulation of predictive models describing treatment performance as functions of governing process design and operating parameters.

Scope

The results presented and discussed in this paper are limited to studies on the removal of degradable organic material by the overland-flow process. The parameters used in this study to measure degradable organic material include five-day biochemical oxygen demand (BOD_5) and total organic carbon (TOC). Thus, in the predictive models formulated as part of this report, treatment performance is described in terms of the reduction in the levels of BOD_5, and TOC.

The limitations of BOD_5 as a model parameter are recognized. However, the objective of this initial modelling effort is to develop a model that can be used directly by engineers as a design aid. Because BOD_5 is the standard parameter specified in discharge requirements and is generally used by consulting engineers as the basis for design of biological systems, this parameter was selected as the basis for the predictive model.

OVERLAND FLOW DESIGN AND OPERATING PARAMETERS

The first step in the development of a rational basis for the design of overland-flow systems is to define the design and operating parameters that may affect process performance and establish units for their expression. A list of the basic design and operating parameters associated with the overland-flow process is presented in Table 1 along with suggested units for their expression and the range of parameter values used in existing systems. A definition of each of these parameters is presented below along with a discussion of current practice.

Slope Length

As defined in this report, the overland-flow slope is the physical surface to which wastewater is applied. It often has been referred to in the literature as a terrace. The overland-flow slope is the reactor where treatment of the wastewater takes place. Prediction of the minimum slope length necessary to achieve a given level of treatment is one of the principal objectives of this study. Slope lengths that have been used successfully for treatment of food processing wastewaters range from 60 to 90 meters, while slope lengths that have been used for municipal wastewater treatment generally range from 30 to 45 meters.

TABLE 1. OVERLAND FLOW DESIGN AND OPERATING PARAMETERS

Parameter	Unit	Typical Range	Range Studied
Slope length, z	meter	30 - 55	0 - 18.3
Slope grade	%	12 - 8	2 - 6
Application period, P	hrs/day	4 - 24	4 - 24
Application frequency	days/wk	3 - 7	5 - 7
Application rate, q	$m^3/(hr \cdot m)$	0.08 - 0.24	0.06 - 0.24
Hydraulic loading rate	cm/day	1 - 7	2 - 11.7[a]

[a] Computed on the basis of 30-m slope length.

Slope Grade

Slope grade is defined as the incline of the slope surface and it is expressed as the percent of vertical rise to horizontal run. Based on experience to date, process performance does not appear to be sensitive to changes in slope grade in the range of 2 to 8 percent [4] [5]. A slope grade in the range of 2 to 6 percent has been recommended by some workers to avoid problems associated with erosion and channeling on steep slopes and ponding on shallow slopes [5].

Slope grades as shallow as ½ percent are used at the Werribee Farm in Melbourne, Australia [6]. However, that system is not comparable to overland-flow systems developed in the United States. Thus, an accurate assessment of the effect of low-slope grades on performance can not be made on the basis of the Werribee experience. Nevertheless, at this time there is no strong evidence indicating that slope grades in the range of ½ to 1 percent would not be suitable for overland flow.

Application Period

Application period refers to the length of time during a day that wastewater is applied to the slope (e.g. 6 hr/day). Most existing systems are operated in the range of 6 to 12 hr/day. Continuous 24 hr/day application periods have been used successfully at a few sites [5] [7], but additional research is necessary to assess long-term effects on performance and the overland-flow slope.

Application Frequency

Application frequency refers to the sequence of application days and non-application days (e.g. 5 day on-2 day off). This is often reported in terms of application days/week (e.g. 5 days/week). Most experimental overland-flow systems are operated on a frequency of 5 or 6 days/week, primarily for reasons of convenience rather than any demonstrated performance effect. Most full-scale systems would be operated on a frequency of 7 days/week except during harvest periods. Extended periods of non-application result in drying of the biological-slime layer which can reduce process efficiency.

Application Rate

Application rate is the volume of wastewater applied to the slope divided by the application time period in hours. To standardize this parameter it is necessary that it be expressed on a per-unit slope-width basis (e.g. in $m^3/(hr \cdot m)$ of slope width). Although this parameter is not often reported in this form, it appears that it is the parameter that has the greatest influence on treatment performance. Application rates used in existing systems range from about 0.06 to 0.24 $m^3/hr \cdot m$.

Hydraulic Loading Rate

Hydraulic loading rate is the volume of wastewater applied per day or per week divided by the area of the overland-flow slope (e.g. cm/day or cm/wk). Rates generally have been reported on a weekly basis. However, expressing the rate on a weekly basis provides no information on how much water is applied each day, which is more important from the standpoint of process performance. Therefore, expression of the hydraulic-loading rate on a daily basis is more meaningful. Historically, this parameter is the one most often reported and has been the design parameter used to determine the land area required for a given system. However, there is evidence (as discussed later) that this parameter, within the range of values commonly used, has much less effect on treatment performance than other parameters. Unfortunately, it has become entrenched in the minds of many as the principal overland-flow design and operating parameter. The probable reason for this is that hydraulic-loading rate is the principal design parameter for conventional irrigation or slow-rate systems, and because the overland-flow process developed as a departure from conventional spray irrigation, it is not unexpected that the design procedures used for the slow-rate process would carry over to the overland-flow process. It should be noted that the hydraulic loading rate can be computed as a secondary, dependent operating variable determined by the independent parameters—application rate, application period, and slope length using the following relationship

$$HLR = \frac{(q)(P)(10^2)}{(z)}$$

where

HLR = hydraulic loading rate, cm/d
q = application rate, $m^3/(hr \cdot m)$
P = application period, hr/d
z = slope length, m

The hydraulic loading rates used in existing systems vary with the nature of the wastewater applied. The rates used for food-processing wastewaters ranged from about 1 to 2 cm/day. Rates used for municipal wastewaters range from about 1 to 2 cm/day for raw wastewater, 1.5 to 3 cm/day for primary effluent, and 1.5 to 6 cm/day for secondary effluent.

INITIAL MODEL DEVELOPMENT

To provide a focus for the experimental work, a preliminary model describing the removal of organic material with the overland-flow process was developed on the basis of theoretical considerations.

In terms of the removal of organic material from wastewater, the overland-flow slope can be considered as a biological film-flow reactor similar in many respects to a trickling filter. The mechanisms responsible for the removal of organic material are the same in both processes. Suspended and colloidal organic matter are separated from the liquid fraction by contact with and subsequent adsorbtion onto the biological-slime layer or film on the surface of the media in the case of trickling filters and on the surface of the soil and vegetation in the case of the overland-flow slope. Contact of the solid particles with the slime layer is brought about by a combination of physical mechanisms including sedimentation and interception. Adsorbed solids are ultimately solubilized by microbial action and the soluble material diffuses into the film where it is converted to end products and new cell material. Soluble organic matter initially present in the wastewater diffuses directly into the biological film.

Because the removal mechanisms in the overland-flow and trickling-filter processes are similar, it is expected that descriptions of organic-removal kinetics also would be similar. On the basis of this expectation, a preliminary model describing the removal of degradable organic material by the overland-flow process is derived below using an approach similar to that presented by Schroeder [8]for the development of the trickling-filter design equation.

Performing a mass balance over an idealized section of the overland-flow slope as shown in Figure 2, and assuming steady-state conditions, the following equation is obtained

$$(Q\,C)_z - N_y w \Delta z = (Q\,C)_{z+\Delta z} \qquad (1)$$

where

Q = flow rate, L/min
C = organic concentration in liquid film, mg/L
N_y = flux of organic material into slime layer, $mg/m^2 \cdot hr$
z = distance down slope, m
w = wetted perimeter, m

If Δz is allowed to approach zero, then:

$$-\frac{d(Q\,C)}{dz} - N_y w = 0 \qquad (2)$$

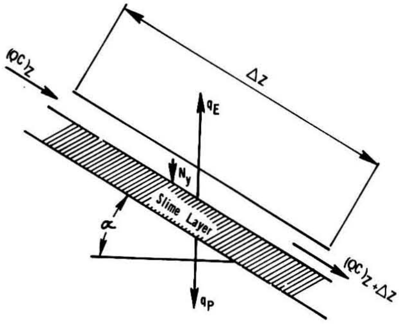

Figure 2. Idealized section through overland-flow slope.

If the flux rate into the slime layer is equal to the reaction rate within the slime layer, the reaction rate follows Monod kinetics, and there is no organic concentration gradient within the liquid film, then the following equation can be written for the flux at the slime surface

$$N_y = \frac{Ek\,C}{Km + C} \qquad (3)$$

where

E = an efficiency factor
k = is a rate constant
Km = is a saturation coefficient

As suggested by Schroeder [*11*], E is approximately proportional to the organic concentration C under normal operating conditions for trickling filters. Thus, we can write

$$N_y = \frac{K_1 C^2}{Km + C} \qquad (4)$$

Because in most cases, $C >> Km$, Equation (4) reduces to

$$N_y = K_1 C \qquad (5)$$

Substitution of Equation (5) into Equation (2) yields

$$\frac{d(Q\,C)}{dz} = -K_1 C\,w \qquad (6)$$

$$C\frac{dQ}{dz} + Q\frac{dC}{dz} = -K_1 C\,w \qquad (7)$$

The term dQ/dz is equal to the loss of water from the system due to peroclation and evapotranspiration. It is assumed that this lost water does not contain organic material. Thus,

$$\frac{dQ}{dz} = -(q_E + q_P)w \qquad (8)$$

where

q_E = evapotranspiration rate, m/hr
q_P = percolation rate, m/hr

Substituting Equation (8) into (7) we obtain

$$Q\frac{dC}{dz} - C\,(q_E + q_P)w = -K_1 C\,w$$

Letting $q_E + q_P = K_2$

$$\frac{dC}{dz} = -\frac{(K_1 - K_2)\,C\,w}{Q} \qquad (9)$$

Integration yields

$$\frac{Cz}{C_o} = \exp\left[-\frac{(K_1 - K_2)\,z\,w}{Q}\right] \qquad (10)$$

where

C_z = organic concentration at a distance z down the slope, mg/L
C_o = organic concentration at the top of the slope mg/L

Water loss from the slope due to evaporation and percolation, as measured by the value of K_2, would increase the concentration of organic matter in the wastewater. According to Equation (10), increasing the value of K_2 would have the effect of reducing the organic-removal efficiency on a concentration basis. It should be noted, however, that increasing the concentration of organic matter would tend to increase the concentration gradient across the film and thus increase the effective rate of removal of organic material. The net effect would be to increase the observed value of K_1 and compensate for the effects of increased K_2. Thus, determination of individual values for K_1 and K_2 would be a very difficult undertaking. In addition, the determination of the wetted perimeter (w) on an overland-flow slope having films on vegetation as well as the soil surface would be impossible. The logical procedure to follow, as suggested by Atkinson [9] in a discussion of trickling filters, is to determine experimentally an overall rate coefficient K that incorporates the individual parameters. Using this empirical approach, Eckenfelder [*10*] proposes a design equation of the following form for trickling filters.

$$\frac{C}{C_0} = \exp\left(-\frac{K\,A_v^{1+m}\,D}{Q^n}\right)$$

The exponents n and m are constants related to the geometry of the medium.

The analogous design equation for the overland-flow process would be of the following form, using units in meters and hours.

$$\frac{C_z}{C_0} = \exp\left(-\frac{Kz}{q^n}\right) \tag{11}$$

where
K = overall rate constant, m/hr
z = distance down slope, m
q = application rate per unit width of slope, $m^3/(hr \cdot m)$
n = empirical constant

Thus, organic-removal efficiency is expressed as a function of distance down the slope and application rate only.

It is interesting to note that similar equations can be derived using a different approach. If it is assumed that organic removal is related to the contact time of the wastewater with the slime layer, and that the organic removal follows first-order reaction kinetics the following relationship can be written

$$\frac{C}{C_0} = \exp\left(-K'T\right) \tag{12}$$

where
K' = reaction-rate constant
T = contact or detention time

The next step in this approach is to determine a relationship between the detention time and other governing operating parameters. Several relationships have been developed to determine the detention time of water flowing on a grass-covered slope. Martel *et al.* [*11*] propose the following equation

$$T = \frac{0.078\,z}{a^{1/3}q} \tag{13}$$

where
T = detention time
z = distance down slope
s = slope grade
q = average flow rate per unit width

Substituting Equation (13) into (12) yields the following organic-removal model

$$\frac{C}{C_0} = \exp\left(-\frac{0.078\,K'z}{s^{1/3}q}\right) \tag{14}$$

Nakano *et al.* [*12*] propose the following equation for the detention time

$$T = \frac{z}{(sc^2q)^{1/3}} \tag{15}$$

where
c = roughness coefficient

Substituting (15) into (12) yields

$$\frac{C}{C_0} = \exp\left[-\frac{K'z}{(sc^2q)^{1/3}}\right] \tag{16}$$

The Soil Conservation Service [*13*] uses the following equation to describe the movement of irrigation water on a vegetated slope.

$$T = \frac{n^{0.6}z}{q^{0.4}\,s^{0.3}} \tag{17}$$

where
n = roughness coefficient

Substituting (17) into (12) yields

$$\frac{C}{C_0} = \exp\left(-\frac{K'z\,n^{0.6}}{q^{0.4}\,s^{0.3}}\right) \tag{18}$$

Equations (14), (16), and (18) are all of the form

$$\frac{C}{C_0} = \exp\left(-\frac{c'K'z}{q^n\,s^m}\right) \tag{19}$$

where
c' = constant related to surface roughness

If the constants c' and K' are combined into a single constant K, then the organic removal described by Equation (19) and the model described by Equation (11) are essentially the same except for the slope-grade term (s^m). This raises the question of whether the slope grade should be a parameter in the model. As indicated previously, it has been shown by several studies that slope grade has had no significant effect on treatment performance. However, these findings cannot be considered conclusive.

Both theoretical and practical questions exist regarding the use of wastewater detention time as the key parameter in a predictive model for organic removal on an overland-flow slope. Detention-time models assume that the overland-flow slope is analogous to a biological plug-flow reactor for which the liquid detention time is the governing operating parameter. However, a plug-flow reactor is a suspended-culture process in which the biological reactions occur in the bulk liquid. As discussed earlier in this section, the overland-flow slope is considered more appropriately as a film-flow reactor in which reactions occur primarily on the soil and vegetative surfaces rather than in the bulk liquid. The important factors affecting the utilization of organic substrate in a film-flow reactor are the contact time of the substrate with the film, the transport rate of substrate to the film surface, and the diffusion rate of substrate and oxygen into the film layer. Bulk-liquid detention time on the slope is important only as it affects these factors. At a given substrate mass-loading or application rate, flow velocity increases and the detention time of the bulk liquid decreases with increasing slope grade according to the hydraulic relationships presented previously. However, at a constant flow rate, the depth of flow also decreases with increasing slope grade and velocity. Shallower liquid depth will tend to enhance the transport of suspended material to the film surface because the solids will have a shorter distance to settle to the surface. Higher flow velocities will tend to reduce the depth of the stagnant liquid layer between the bulk liquid and the film surface, thereby reducing the substrate concentration gradient between the bulk liquid and the film surface and maintaining a higher substrate concentration at the film surface. The diffusion rate of substrate into the film would be expected to depend on the substrate concentration at the film surface and this assumption is supported by the work of Williamson and McCarty [*14*]. Based on these considerations, it would appear that, although liquid detention time and, therefore, contact time decrease with increasing slope grade, the corresponding reduction in flow depth may enhance the rate of substrate utilization and off-set the effect of reduced contact time. Thus, the effect of slope grade on organic-removal efficiency may be nil or much less than predicted by its effect on detention time alone.

From a practical standpoint, the use of a predictive model based on detention time is somewhat cumbersome. First of all a correlation must be developed between detention time and organic-removal efficiency. Detention time must be estimated by means of tracer studies, and the value will change with application rate, slope length, temperature, and possibly other variables. The detention time thus determined is not an exact value, but depends on the type of tracer, the procedures used in the study, and the method used to determine the detention time from the tracer response data. To verify the model at other overland-flow sites, a standard procedure for conducting tracer studies would have to be established. For the model to be of practical benefit, a correlation also must be developed between detention time and measurable design and operating parameters, such as application rate and slope length. Since the net result of the detention-time model is an empirical correlation between organic-removal efficiency and the design and operating parameters, it would seem that a simpler and more direct approach to model development would be to eliminate consideration of detention time and develop direct correlations between organic-removal efficiency and the measurable design and operating parameters. The net relationship would be the same and model verification at other overland-flow systems would be less involved.

It is important to note that the hydraulic loading rate does not appear as a parameter in either form of the removal model derived above. The application rate is the only operating variable that appears in the model. As discussed previously, hydraulic-loading rate historically has been used as the principal design parameter for the overland-flow process and relationships between hydraulic-loading rate and treatment performance have been suggested [*15*]. Thus, the question is raised as to whether the hydraulic-loading rate should be included as a model parameter.

The preliminary models derived above and the questions raised about the parameters to be included in the model provide a focus for the pilot studies. Questions to be answered by the pilot studies include the following:

1. Can removal of organic material by the overland-flow process be described as an exponential decay function of distance down the slope?
2. What is the effect of application rate on organic-removal efficiency?
3. What effect, if any, does slope grade have on organic-removal efficiency?
4. What effect, if any, does hydraulic-loading rate have on organic-removal efficiency?

The answers to these questions will provide a basis for the development of a predictive model describing removal of organic material by the overland-flow process.

PILOT STUDY FACILITIES

The experimental overland-flow slopes and associated equipment were housed indoors in the Civil Engineering laboratory at the University of California, Davis. The major components of the pilot facilities include three overland-flow slopes, artificial light banks, and a wastewater feed system. A schematic flow-diagram of the pilot study facilities indicating the arrangement of system components is shown in Figure 3. Details of the facilities appear in other publications [*16*].

PILOT STUDY PROCEDURES AND RESULTS

Pilot studies were conducted in two phases. The first phase involved treatment studies with synthetic soluble wastewater and the second phase involved studies with primary treated municipal wastewaters. The same basic experimental approach was used in both phases of the study. The objectives of the study, as outlined previously, were to identify the design and operating parameters that affect overland-flow process performance and to develop functional relationships between these governing parameters and process performance. On the basis of previous experiences and the initial models developed previously, the parameters slope length, slope grade, application rate, and hydraulic-loading rate were identified as probable or potential governing parameters. Therefore, the basic study approach was to devise and conduct treatment tests that would reveal the nature of the effect of each parameter on process performance. The treatment test procedure used to achieve this consisted of operating the three beds so as to vary one operating parameter while holding all others constant. The parameters slope grade, application rate, and hydraulic-loading rate were tested in this manner. The effect of slope length was studied as part of all experiments by taking samples of the surface flow at intervals down the slope and analyzing for organic material. The beds also were operated in series to determine the effect of longer slope lengths on process performance. Each experiment was conducted for a period of 4 to 8 weeks or until no trends in treatment performance were observed. The details of each treatment study are described below.

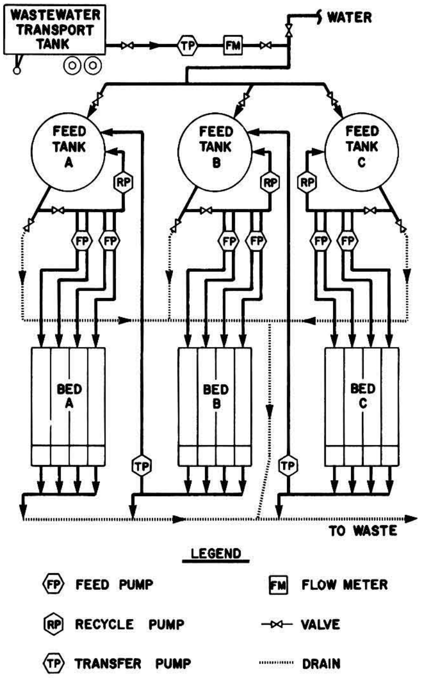

Figure 3. Overland-flow pilot facilities flow diagram.

Synthetic Wastewater Studies

Synthetic wastewater was used to study the effects of slope grade, application rate, and hydraulic-loading rate on organic-removal efficiency by overland flow. Only the slope grade study is reported here. Results from the other synthetic wastewater studies are reported in another publication [*16*].

Prior to starting any treatment studies, wastewater was applied to the beds under the same operating conditions, to allow a slime layer to build up on the slopes. This slope acclimation was continued for about 2 months until the effluent quality from all three beds was consistent and equal.

Wastewater Characteristics

The synthetic wastewater used in this study was prepared according to the following recipe:

sucrose – 174.4 mg/L
bactopeptone – 49.7 mg/L
NH_4Cl – 69.4 mg/L
KH_2PO_4 – 21.8 mg/L
$K_2HPO_4 \cdot 3H_2O$ – 31.9 mg/L

Synthetic wastewater characteristics, as measured by analytical tests, are listed in Table 2. Because the wastewater was pumped through several feet of tubing prior to application, the characteristics of the wastewater discharged from the distribution manifold varied slightly from day to day.

Slope-Grade Study

A study to determine the effect of slope grade on removal of organics involved operating the beds at three different slope grades (2, 4, and 6 percent) while holding all other operating parameters constant. The other operating conditions used during the slope-grade studies are indicated in Figure 4. It should be noted that the application rate used in these studies is in the range used in full-length overland-flow systems. Thus, the 6.1-m experimental beds used in these pilot studies were intended to simulate the first 6.1-m of a longer overland-flow slope. The resulting hydraulic loading rates computed on the basis of the 6.1-m slope length were much higher than the rates normally associated with full-length systems. To allow the hydraulic loading rates used in this study to be more easily compared with rates used in existing full-length systems, the hydraulic loading rates used in this study were computed on the basis of a 30-m slope length and are expressed in units of cm/day/30 m. The hydraulic-loading rates based on the actual slope length of 6.1 m would be roughly 5 times the rate computed on the basis of a 30-m slope length.

Samples were taken at several points along the length of the slope and were analyzed for BOD_5 and TOC. The slope-grade study was conducted for a period of 8 weeks.

The fraction of organic material remaining in terms of TOC is plotted on a semi-log scale as a function of down-slope travel distance in Figure 4 for the three slope grades studied (2, 4, and 6 percent). The data points shown are mean values of the fraction remaining and the lines shown are statistically determined lines of regression forced to pass through the point (0,1). A summary of the resulting regression equations and correlation coefficients is presented in Table 3. Similar results were obtained for BOD_5 and are reported in Reference [*16*].

The regression coefficients are the slopes of the regression lines and represent the rates of change with distance of the fraction of organic material remaining. The regression coefficients were tested for homogeneity, and no significant differences among regression coefficients were found at the 5-percent level for the TOC case. On the basis of the results presented above and similar findings reported from studies at Pauls Valley, OK [*17*] and Utica, MS [*4*], it was concluded that slope grade in the range of 2 to 6 percent should not be included as a parameter in an overland-flow organic-removal model. Consequently, a slope-grade study was not conducted with primary effluent.

TABLE 2. CHARACTERISTICS OF APPLIED WASTEWATERS, MG/L

Constituent	Synthetic Wastewater	Primary Effluent
BOD_5	135-145	65-100
TOC	90-100	40-60
TOD	—	200-250
Suspended solids	0	80-90
Total N	23-25	28-32
NH_3-N	12-14	20-24
NO_3-N	0	<0.1
Total-P	10	—
pH	7.5-8.0	7.5-8.0

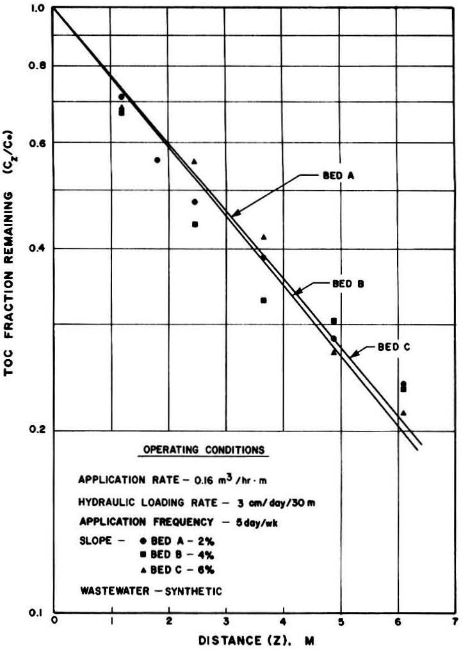

Figure 4. TOC fraction remaining vs. down-slope distance—Synthetic wastewater slope-grade study.

Primary Effluent Studies

Studies to determine the effects of application rate, hydraulic-loading rate, and slope length were conducted using primary effluent from the City of Davis wastewater-treatment plant. Prior to starting treatment studies with primary effluent, primary effluent was applied to the beds under the same operating conditions to acclimate the slopes to the change in wastewaters. Approximately one month of acclimation was required to produce a consistent effluent from all three beds. A considerable amount of unloading of the slime layer that was built up during the synthetic wastewater studies occurred during the initial stages of acclimation. This would indicate a significant change in the nature of the bacterial population on the slopes.

Wastewater Characteristics

Primary effluent from the City of Davis wastewater-treatment plant was used for all studies reported here. Primary effluent was pumped from the effluent channel of the primary tanks into a 2,800-liter tank truck and transported daily to the pilot study facilities. At the laboratory, specified volumes of wastewater were metered into the feed tanks. Excess wastewater was drained to waste. All wastewater was applied on the same day it was transported. The characteristics of the primary effluent from the City of Davis Plant are indicated in Table 2.

Application Rate Study

A study to determine the effect of application rate on removal of organics was conducted by operating the beds at three different application rates (0.08, 0.16 and 0.24 $m^3/(hr \cdot m)$) while holding the other parameters constant the except application period. To maintain a constant hydraulic loading rate while varying the application rate, it is necessary to vary the application period as well. The resulting application periods associated with the different application rates were approximately 12, 6, and 4 hours/day, respectively. The other operating conditions used in this study are indicated in Figure 5.

Table 3. Summary of Regression Parameters for Synthetic Wastewater Slope Grade Study

Measured Parameter	Slope Grade, %	Regression Coefficient	Regression Equation*	Correlation Coefficient, r
TOC	2	-0.259	$C_z/C_0 = e^{-0.259\,(z)}$	0.973
	4	-0.264	$C_z/C_0 = e^{-0.264\,(z)}$	0.973
	6	-0.258	$C_z/C_0 = e^{-0.258\,(z)}$	0.987

* z in meters.

Samples were taken at several points down the length of the slope and analyzed for BOD_5 and TOC. The application rate study was conducted over a period of 8 weeks.

The results are presented in the form of a semi-log plot of BOD_5 fraction remaining versus travel distance down the slope and are shown in Figure 5. The data points shown represent mean values of the fraction remaining and the lines are regression lines forced to pass through the point (0,1). A summary of regression coefficients and equations and correlation coefficients are presented in Table 4. The average concentration of suspended solids in the effluent from each bed is presented in Table 5.

On the basis of the initial organic-removal models developed previously, the expected relationship between application rate (q) and organic-removal efficiency is that given by Equation 11.

$$\frac{C_z}{C_0} = \exp\left(-\frac{Kz}{q^n}\right) \tag{11}$$

The form of this relationship is strongly supported by the results of the primary effluent application rate study. Using graphical techniques described in another publication [*16*], values were determined for the exponent n and the rate constant K that appear in Equation 11. For the BOD case the values of n and K are 0.48 and 5.82 × $1-^{-2}$ m/hr. Substituting these values into the model (Equation 11) yields the following predictive relationship for the removal of BOD_5 from primary effluent

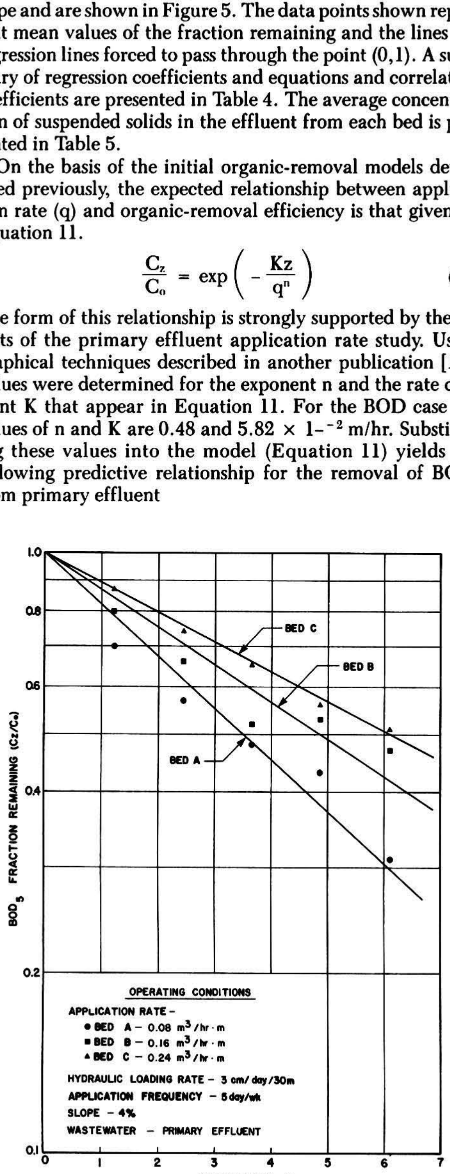

Figure 5. BOD_5 **fraction remaining vs. down-slope distance—primary effluent application-rate study.**

BOD Removal Model

$$\frac{C_z}{C_0} = \exp\left[-\frac{5.82 \times 10^{-2}\,(z)}{q^{0.48}}\right] \tag{20}$$

These equations are valid for q in the range of 0.08 to 0.24 $m^3/(hr \cdot m)$ and for z in the range of 0 to 6 m.

Hydraulic Loading Rate Study

A study to determine the effect of hydraulic loading rate on removal of organics was conducted by operating the beds at three different hydraulic-loading rates (2, 3, and 6 cm/day/30 m) while holding the other parameters constant except application period. To maintain a constant application rate while varying the hydraulic-loading rate, it is necessary to vary the application period as well. The resulting application periods associated with the different hydraulic-loading rates were approximately 4, 6, and 12 hours/day. The other operating parameters used in this study are indicated in Figure 6. Samples were taken at several points along the length of the slope and were analyzed for BOD_5 and TOC. The hydraulic-loading rate study was conducted for a period of 5 weeks.

A semi-log plot of BOD_5 fraction remaining versus travel distance down the slope is shown in Figure 6. The data points shown are mean values and the lines are regression lines forced to pass through the point (0,1). A summary of regression coefficients and equations and correlation coefficients is presented in Table 4. Effluent suspended solids data are shown in Table 5.

Changes in hydraulic-loading rate of the primary effluent had little or no effect on process performance in terms of BOD removal. No significant differences at the 5-percent level were found between the regression coefficients associated with the 6 and 3 cm/day/30 m loading rates. The regression coefficients for the 2 cm/day/30 m loading rate were found to be significantly different statistically at the 1-percent level from the coefficients for the other rates, but the differences are small and would be considered insignificant from the standpoint of practical process control. These results confirm the form of the initial model (Equation 11) which states that process performance is independent of hydraulic-loading rate.

Extended Length Study

To determine the effect of longer down-slope travel distance on organic removal, a study was conducted by operating the three beds in series. Primary effluent was applied in the usual manner to Bed A. Effluent from Bed A was discharged into a collection sump and pumped back to Feed Tank B. The water in Feed Tank B was then applied to Bed B in the usual manner and at the same rate used for application to Bed A. Effluent from Bed B was transferred to Feed Tank C and applied to Bed C in the manner just described. Effluent from Bed C was drained to waste in the usual manner. By operating the beds in series in the above manner, a total slope length of 18.3 m was achieved. The operating conditions used in this study are indicated in Figure 7.

Samples were taken in the usual manner from Bed A, but only from the effluent trays of Beds B and C. Samples were analyzed for BOD_5, TOC, TOD, and suspended solids. The study was conducted for a period of 6 weeks.

TABLE 4. SUMMARY OF REGRESSION STATISTICS FOR BOD REMOVAL PRIMARY EFFLUENT STUDIES

Parameter Studied (units)	Parameter Value	Regression Coefficient	Regression Equation[a]	Correlation Coefficient, r
Application rate ($m^3/(hr\cdot m)$)	0.08	-0.197	$C_z/C_o = e^{-0.197\,(z)}$	0.971
	0.16	-0.142	$C_z/C_o = e^{-0.142\,(z)}$	0.968
	0.24	-0.116	$C_z/C_o = e^{-0.116\,(z)}$	0.983
Hydraulic loading rate (cm/day/30 m)	2	-0.158	$C_z/C_o = e^{-0.158\,(z)}$	0.987
	3	-0.142	$C_z/C_o = e^{-0.142\,(z)}$	0.982
	6	-0.147	$C_z/C_o = e^{-0.147\,(z)}$	0.984

[a] z in meters.

TABLE 5. SUMMARY OF AVERAGE EFFLUENT SUSPENDED SOLIDS CONCENTRATIONS MEASURED DURING PRIMARY EFFLUENT STUDIES

Parameter Studied	Parameter Units	Parameter Value	Effluent Suspended Solids, mg/L
Application rate	$m^3/(hr\cdot m)$	0.08	14.2
		0.16	24.7
		0.24	25.9
Hydraulic loading rate	cm/day/30 m	2.0	27.0
		3.0	25.0
		6.0	30.0
Extended length-distance	meters	6.1	26.8
		12.2	25.0
		18.3	17.0

A semi-log plot of BOD_5 remaining versus travel distance down the slope is shown in Figure 7. The data points shown are mean values. It can be seen from the data points shown in Figure 7 that the rate of organic removal observed over the first few meters of travel is significantly greater than the removal rate observed over the remaining length of slope. Considering this observed difference in removal rates over different portions of the slope, a more appropriate description of the removal of organic material from primary effluent by overland flow would be a two-stage or composite model. The first stage of the model would apply over the first few meters of the slope and the second stage would apply over the remainder of the slope. The first stage of the model is of the same general form as the models described previously (Equation 11).

$$\frac{C_z}{C_o} = \exp\left(-\frac{Kz}{q^n}\right)$$

Values for the coefficients, K and n, for the BOD-removal model were determined as part of the primary effluent application rate study and are indicated in Equation 20.

The second stage of the composite model is of the form

$$\frac{C_z}{C_o} = A\exp\left(-\frac{K'z}{q^{n'}}\right) \tag{21}$$

The coefficient A is the value of C_z/C_o where the second-stage regression line intersects the vertical axis as indicated in Figure 7. Because the extended-length study was conducted at a single application rate, values for the coefficients K and n could not be determined from the available data. To generate the data necessary to determine values for these coefficients, full-length overland-flow slopes must be operated in parallel at several different application rates. Such studies are planned as part of the Phase II field studies. Regression equations for the Stage 2 curves shown in Figure 7 can be written. However, the equations are applicable only under the operating conditions indicated on the figure. The Stage 2 regression equation for BOD removal is

$$\frac{C_z}{C_o} = 0.72\exp\left[-8.1\times10^{-2}\,(z)\right] \tag{22}$$

where
z = slope length, m

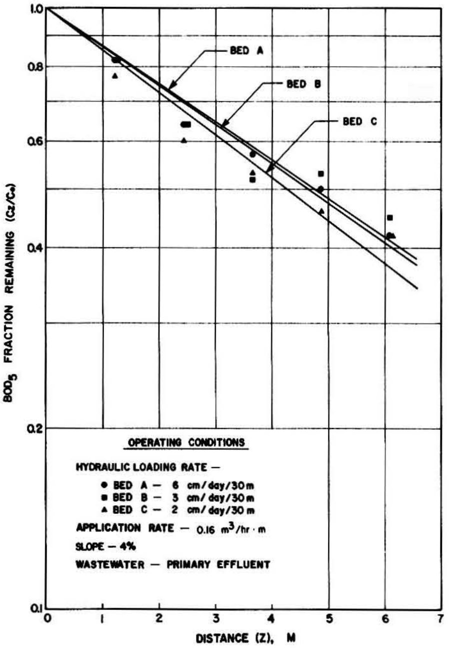

Figure 6. BOD_5 fraction remaining vs. down-slope distance—primary effluent hydraulic rate loading study.

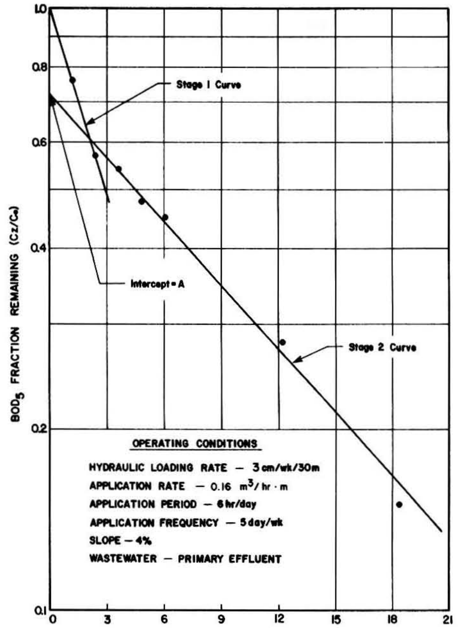

Figure 7. BOD_5 **fraction remaining vs. down-slope distance—two-stage BOD-removal model.**

To confirm the validity of the two-stage model concept, a test was conducted on a full-length slope at the overland-flow research facility operated by the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, N.H. The test consisted of operating two parallel slopes at an application rate of 0.12 $m^3/(hr \cdot m)$ and taking grab samples of surface flow at several locations down the length of each slope. The samples were collected and analyzed by CRREL personnel and reported to U.C. Davis. The regression equation determined from the CRREL data is

$$\frac{C_z}{C_o} = 0.72 \exp\left[-5.6 \times 10^{-2} (z)\right] \qquad (23)$$

where
z = slope length, m

This equation is of the same general form as Equation (22) from the extended-length study.

DISCUSSION

The discussion presented below is focused on the development of a predictive model to describe the removal of organic material in wastewater with the overland-flow process and the use of the model as a rational basis for the design and operation of overland-flow systems.

Elements of a Predictive Model

Several overland-flow designs and operating variables were identified as potential parameters to be included in a predictive model describing the removal of organics with the overland-flow process. A list of these parameters and the units for their expression are presented in Table 1. The effect of these parameters on organic removal was studied by observing changes in organic-removal efficiency in response to changes in the value of each parameter. The range of values studied for each parameter is indicated in Table 1.

From the studies reported herein, it was found that removal of organic material from primary municipal effluent by overland-flow is independent of slope grade, application period, application frequency, hydraulic-loading rate and organic-loading rate, and is dependent only on the parameter slope length and application rate. Of course, these findings apply only over the range of parameter values studied, as indicated in Table 1. In addition, it was found that removal of organic material from primary effluent can be described by a two-stage model that is a function only of slope length (z) and application rate (q). The model is expressed in the following form.

$$\frac{C_z}{C_o} = \exp\left(-\frac{Kz}{q^n}\right) \qquad \text{(Stage 1)}$$

$$\frac{C_z}{C_o} = A \exp\left(-\frac{K'}{q^{n'}}\right) \qquad \text{(Stage 2)}$$

where
C_o = influent organic concentration
C_z = organic concentration at a distance z down-slope
K,K' = empirically determined rate constant, m/hr
z = distance down-slope, m
q = application rate, $m^3/(hr \cdot m)$
n,n' = empirically determined coefficient
A = empirically determined coefficient

The two-stage model for BOD_5 removal is illustrated in graphical form in Figure 7. The first stage of the model applies to the first 3 to 6 m of slope length, where the rate of organic removal is most rapid. Stage 2 of the model applies over the remainder of the slope. From a practical design and operation standpoint, the first stage of the model would be of little importance, and the second stage of the model would serve as the basis for design and operation.

The probable reason for the observation of two distinct rates of organic removal over the length of the overland-flow slope is that larger suspended matter is removed readily in the first few meters, leaving colloidal and soluble organic material to be removed at a slower rate over the remaining length of the slope. This hypothesis is supported by results from the effluent characteristics study and the CRREL field test, in which it was shown that most of the organics removed in the first 4 to 6m of travel were filterable. In addition, it was found from the CRREL test that most of the suspended solids were removed in the first few meters of travel.

Values for the empirical coefficients (K and n) in Stage 1 of the model were determined on the basis of 6m of down-slope travel (see Equation 20). Values for K' and n' in the Stage 2 equation could not be determined because extended-length studies were only conducted at a single application rate. An application-rate study needs to be conducted on parallel, full-length slopes to determine values for K' and n'. Because n is related to the hydraulic characteristics of the slope, the values of n and n' are expected to be similar. The value of the rate constant for the first stage (K) should be greater than the rate constant for the second stage (K'), because the observed rate of removal is more rapid over the first few meters.

An important feature of the proposed model is that application rate, not hydraulic-loading rate, is the principal variable in the model. This feature is important because the hydraulic-loading rate, historically, has been the principal parameter used in the design of overland-flow systems, and it generally has been thought that process performance was related to hydraulic-loading rate. Thus, a predictive model based on application rate rather than hydraulic-loading rate is a major departure from current thinking regarding overland-flow design and operation.

Exclusion of hydraulic-loading rate as a model parameter is supported by the recent work of Martel *et al.* [11] at the CRREL facility in Hanover, New Hampshire. This research group also has proposed a model for organic removal by overland flow that does not contain hydraulic-loading rate as a model parameter. Details of the CRREL model were described previously in the section on initial model development. However, there are important differences between the CRREL model and the one developed in this report (the UCD model). The CRREL model is based on combined relationships among wastewater detention time on the slope, treatment efficiency, and the parameters; application rate, slope length, and slope grade. In contrast, the UCD model is not based on detention time, rather on a direct relationship between treatment efficiency and the parameters application rate and slope length. Slope grade is not a parameter in the UCD model. Arguments for eliminating detention time from the model are presented in the section on initial model development. Elimination of slope grade as a model parameter is based on arguments presented in the section on initial model development and confirming experimental results from this and other studies [*4*], [*5*], and [*16*].

Although the model developed here is empirical, it has a theoretical basis. Considering the complexity of the soil-microbe environment and the current limited knowledge of the interactive process that occur in that environment, the only possible approach to overland-flow model development that can be taken at this time is empirical. The model developed here is straightforward and, after field verification, should be useful as a general design tool.

ENGINEERING SIGNIFICANCE

The findings presented here and the models developed on the basis of these findings have several important implications with respect to the design and operation of overland-flow systems used for removal of degradable organic material and suspended solids from municipal wastewaters. A rational overland-flow design and procedure based on the proposed organic-removal model is presented and illustrated by a numerical example. In addition, general design and operating guidelines derived from the pilot studies are set forth.

Rational Design Approach

Under current overland-flow design procedures, the hydraulic-loading rate is the principal design and operating parameter. It has been shown through studies reported here that organic-removal efficiency is independent of the hydraulic-loading rate within a range of values that include those typically used in existing systems. It was further shown that organic-removal efficiency depends only on the slope length and the application rate. The model developed to describe organic removal is a function only of these two variables. Such a rational approach to overland-flow design based on these findings is described below.

General Design Procedure

The general form of the Stage 2 equation of the proposed organic-removal model is

$$\frac{C_z}{C_o} = A \exp\left(- \frac{Kz}{q^n} \right) \qquad (24)$$

as described previously. The model contains two variables, application rate (q) and slope length (z), either of which may be used as the initially selected or independent design variable. When designing a system, the required or desired level of treatment is known. Thus, a value for (C_z/C_o) can be established. If slope length is used as the independent variable, then a design value for slope length (z) is selected and substituted into Equation (24) along with the known value of C_z/C_o. The required value of application rate (q) is then computed using Equation (24). Alternatively, if application rate is the independent design variable, then a value of q is selected and substituted into Equation (24), and the required value of slope length (z) is computed using the equation. Which parameter to use as the independent design parameter depends on the individual case. Site conditions may dictate the allowable slope length, in which case slope length would be the independent parameter and application rate would be the computed parameter. If slope length is not restricted, then application rate should be used as the independent parameter.

To complete the design of a system, the total area required for slopes must be determined. Total area required may be computed using the following equation, assuming an application frequency of 7 days/week.

$$\text{Area} = \frac{(Q)\,(z)}{(q)\,(P)} \qquad (25)$$

where

Q = average daily flow, m^3 day
k = slope length, m
q = application rate, $m^3/(hr \cdot m)$
P = daily application period, hr/day

For a given removal efficiency the required area may be written as a function only of slope length or only of application rate by combining Equations (24) and (25). Performing this combination yields the following relationships:

$$\text{Area} = \frac{Q \left[-\ell n \left(\frac{C_z}{A\,C_o} \right) \right] (q^{n-1})}{(P)\,(K)} \qquad (26)$$

and

$$\text{Area} = \left(\frac{Q}{P} \right) \left[\frac{K}{-\ell n \left(\frac{C_z}{A\,C_o} \right)} \right]^{1/n} z^{(1-1/n)} \qquad (27)$$

The value of n in the Stage 1 equation was shown to be less than 1 (approximately 0.5 for BOD removal). It is expected that the value of n in the Stage 2 equation will be similar. Assuming that the value of n is less than 1, the value for the area given by either Equation (26) or (27) will be minimized when either q or z are maximized. Therefore, the recommended design approach is to select the maximum application rate within the valid region of the model (see Table 1) and compute the required slope length using Equation (24). If the computed slope length is greater than that allowed by the site conditions, then the maximum allowable slope length should be selected and the required application rate computed.

The parameter, application period (P), is an independent parameter to be selected by the designer and does not affect treatment efficiency according to the model. According to Equation (25), the area will be minimized when P is a maximum. The maximum application period, of course, is 24 hrs/day (continuous application). As indicated earlier, the use of continuous application may result in crop damage when the application rate is above a certain, but as yet unknown, value. Thus, selection of P must be based on previous successful experience. Application periods up to 12 hrs/day were used in the primary effluent studies without any apparent adverse affects on the cover crop. Additional field testing will be necessary to define more clearly suitable or safe values of P at given application rates. The effect of the application period on nitrogen removal is not considered in this dicussion. If nitrogen or ammonia removal is a design consideration, then the application period may be dictated by nitrogen-removal requirements because nitrogen transformations are known to be sensitive to changes in application period.

Design Example

The following numerical example is presented to illustrate the design procedure just described.

Assume the following information is known:

1. Average flow (Q) = 3,000 m^3/day
2. Influent BOD_5 (C_o) = 200 mg/L
3. Required effluent BOD_5 (C_z) = 20 mg/L
4. Stage 2 model coefficients

$A = 0.72$
$n = 0.50$
$K = 1.90 \times 10^{-2}$ m/hr

The necessary design calculations are:

1. Compute the required removal ratio C_z/C_0.

$$\frac{C_z}{C_0} = \frac{20}{200} = 0.10$$

2. Select maximum value of the application rate (q) in the valid range of the model.

$$\text{Select } q = 0.24 \text{ m}^3/(\text{hr} \cdot \text{m})$$

3. Compute the required value of slope length (z) using Equation (26).

$$\frac{C_z}{C_0} = \exp\left(-\frac{Kz}{q^n}\right)$$

$$z = \left(-\ell n \frac{C_z/C_0}{A}\right)\left(\frac{q^n}{K}\right)$$

$$= \left(-\ell n \frac{0.1}{0.72}\right)\left(\frac{0.24^{0.5}}{0.019}\right)$$

$$= 50 \text{ m}$$

4. Select application period (P).

$$P = 12 \text{ hrs/day}$$

5. Compute required total area. Assume 7 day/week applications frequency.

$$\text{Area} = \frac{(Q)\ (z)}{(q)\ (P)}$$

$$\text{Area} = \frac{(3{,}000 \text{ m}^3/\text{day})\ (50\text{m})}{(0.24 \text{ m}^3/(\text{hr} \cdot \text{m}))\ (12\text{h})}$$

$$\text{Area} = 52{,}083 \text{ m}^2 = 5.2 \text{ ha}$$

The required area of 5.2 ha is considerably less than would be calculated using existing design criteria. Using 3 cm/day as the typical hydraulic-loading rate currently used for design, an area of 10 ha would be calculated. The implication is that current design criteria may be quite conservative. However, judgment on the question of the conservatism of current design criteria must be withheld until the proposed organic-removal model can be tested and verified in the field.

The design procedure outlined above meets the objective of providing a rational approach to the design of overland-flow systems. Once fully verified by field testing, this procedure will provide a basis for optimizing overland-flow design.

Design and Operating Guidelines

The following general guidelines for overland-flow design and operation are based on the findings from the Phase I pilot studies. The guidelines are based on treatment of municipal primary effluent, but are also expected to be valid for screened raw municipal wastewater.

1. Removal of organic material is independent of slope grade in the range of 2 to 6 percent. Thus, slope grade is not a critical design parameter in this range.
2. Removal of organics from primary effluent by overland flow is independent of hydraulic-loading rate and application period, and is dependent only on application rate and slope length. Therefore, the following effects can be expected.
    a. The hydraulic-loading rate can be increased on a given slope without affecting the organic-removal efficiency. This can be accomplished by increasing the period of application while maintaining a constant application rate.
    b. Decreasing the application rate will improve the organic-removal efficiency over a given length of slope.
    c. Improved organic-removal efficiency can be achieved on a given slope without reducing the hydraulic-loading rate by decreasing the application rate and increasing the application period.
3. Removal of organics from primary effluent is independent of temperature in the range of 18 to 28°C.
4. Design of overland flow systems should be based on the parameters application rate, slope length, and application period, rather than on the hydraulic-loading rate.

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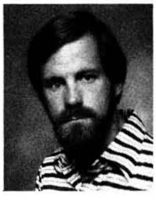

R.G. Smith worked as project engineer for Metcalf and Eddy, Inc. from 1970 to 1976. During this period, he spent a major part of this time on land treatment systems, including development and writing of the USEPA process design manual for **Land Treatment of Municipal Wastewater.** He has served as a principal author on the second edition of the manual which was released recently. Since 1978, he has served as Associate Development Engineer for the Department of Civil Engineering, University of California, Davis, directing research on the overland flow process. He holds a BSCE, and MSCE from Stanford University and a Ph.D from the University of California at Davis.

Pollutant Transport in Wetlands

Marshes, bogs, or other types of wetland prove to be excellent receivers for the disposition of treated wastewaters containing small amounts of dissolved nitrogen and phosphorus.

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Treated wastewater contains small amounts of dissolved nitrogen and phosphorus, in the form of nitrate, ammonium, and phosphate ions, as well as dissolved non-ionic forms. These fertilizers cause eutrophication of any ecosystem receiving them. A marsh, bog, or other wetland type is a feasible recipient because of low human use and acceptability of additional plant and algal growth in such an environment.

Water flow in wetland ecosystems frequently occurs in thin-sheet flows (5-20 cm deep), at slow rates (*ca.* 100 meters per day). This permits intimate contact between the water and the soil-litter horizon. The mechanisms for nutrient removal include mass transfer to the soil and sorption thereon. Subsequently, plants and algae utilize these compounds, incorporating them in tissues which later become litter in the case of plants, and sediments in the case of algae. These in turn slowly decompose, releasing some of the nutrients, but also retaining a portion in the litter or newly formed soil.

Another major function performed by these ecosystems is the removal of suspended sediments from water as it moves through the wetland. The suspended material reaching the wetland joins large amounts of naturally-generated suspendable materials, and both are transported by surface waters. Sedimentation and physical filtration occur enroute, as does "generation" of suspended material by biological activities both above and below the water surface. For example, algal debris may form at one location and be deposited somewhere downgradient in the peatland.

These mechanisms represent a simplification of a more complex system, which involves interconversions due to bacteria, and consumption by aquatic invertebrates. However, processes involving these lower trophic levels take place at rates which are measured in hours, and cannot be interpreted easily in a complex ecosystem.

Figure 1 shows the processes under discussion in schematic form. It can be seen that the formation of litter or soil requires intermediate steps of the uptake of the material by living plants, their subsequent senescence, and the accompanying litter fall. The time delays occasioned by these intermediate steps are not long if one is considering year-to-year variations. On the other hand, they do create a "sink" at the soil water interface. These processes, when coupled with the adsorption of nutrients upon the soil itself, give rise to a very low concentration of a dissolved species at the soil-water interface. Thus, the short-term process of the transport of a dissolved species to the surface may be considered to be limited by mass transport from the bulk flowing water to the soil surface.

The focus of this paper is on the transport mechanisms.

TRANSPORT/CONSUMPTION PROCESSES

The removal of a wastewater component, such as phosphorus, from the surface-water sheet can be envisioned as a two-step process. First, phosphorus must be transported to some consuming entity or compartment within the stationary ecosystem. For solutes, this is accomplished by bulk water flow, by diffusion, and by convective mass transfer. For suspended material, the nature of the water flow and the settling behavior will determine the delivery rate. Once delivered, phosphorus must then be consumed and incorporated into the stationary ecosystem, this step also proceeds at a finite rate. The major consumption mechanisms for nutrients and heavy metals are plant uptake, sorption, soil building, and microbial reactions. In this case, consumption is defined as the net removal of wastewater components from surface waters, after accounting for seasonal cycles. If the transport and consumption rates differ greatly, the slower step will dictate the overall removal rate.

Transport depends largely upon the characteristics of the surface-water sheet, such as depth, flow rate, and component concentrations. Thus, given similar hydrological conditions, the transport rate of material to the stationary ecosystem should not vary seasonally. The consumption mechanisms however, such as adsorption and the production of new biomass, can exhibit saturation phenomena. Therefore, the rate at which the consumption steps progress may slow with time for wetland areas exposed to wastewater.

WETLAND WATER FLOW

The rate at which water can flow across a wetland is controlled by the ground slope, water depths, type of vegetation, and by the degree and type of channelization. The flow is not

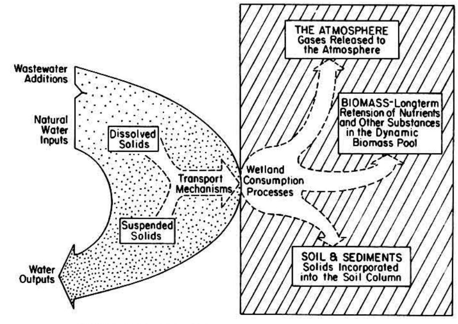

Figure 1. Transport and consumption of pollutants in a wetland.

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only related to water depth by the water-balance equation, but also by an appropriate expression which relates the water velocity to driving forces (hydraulic gradient) and resistances.

Typical water depths in a wetland may range from a few centimeters to about one meter. Spatial variations in depth within a wetland are largely due to changes in the elevation of the underlying soil. The water pool is relatively flat with very small surface gradients. Wastewater, introduced to the wetland, will spread from the discharge points and, if the irrigation rate is sufficiently high, a shallow mound of water will form. This mound will not generally exceed about 10 centimeters, but the height will be determined by the discharge rate and the piping configuration.

The water will move away from the discharge through the wetland vegetation, which presents an obstruction to flow. This vegetative mat comprises a doubly porous medium, with plant stems and litter forming fine-scale porosity, while hummocks, islands, and channels cause a coarse-scale porosity.

The movement of surface waters through wetlands is characterized by very low velocities, which result in developing streamline flow. When considering a momentum balance, under these conditions the inertial and acceleration terms are negligible with respect to frictional and gravitational effects. Flow therefore proceeds at the rate at which gravitational forces are just counterbalanced by frictional drag forces.

Although a great deal of work has been done on overland flow (e.g., Woolhiser and Liggett [*1*]), most have not addressed the problem of point or line water discharges. These geometries are the common approach to wastewater irrigation in wetlands. The functional dependence of water velocity upon depth and gradient in wetlands has been studied by Kadlec, *et al.* [2]. For a point discharge, the material balance for radial flow can be represented by

$$\frac{[\partial \phi_s h]}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}[rh\phi\ v] = p - e - i \tag{1}$$

It should be noted that there can be a difference between the porosity for water storage and the pore space available for water flow. This is illustrated in Figure 2. Water may soak into hummocks, for example, but they still provide an obstacle to overland flow. The apparent porosities can be expected to vary with water depth, but little quantitative information is available. Various forms can be assumed for the friction law, to replace ϕv in Equation 1 in terms of h and $\partial h/\partial r$ and thus allow solution. If the hydraulic radius is assumed to be the channel depth rather than the typical size of an obstruction, a power-law flow expression results:

$$\phi v = -ch^2 \frac{\partial h}{\partial r} \tag{2}$$

Kadlec, *et al.* [2] determined solutions to Equations 1 and 2, and showed that field data could be reasonably represented.

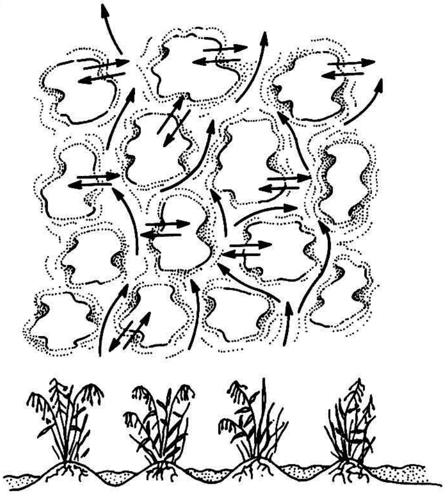

Figure 2. Details of local water movement in a wetland.

TRANSPORT OF DISSOLVED SOLIDS

In wetland areas where no saturation with nutrients or heavy metals has occurred, removal rates for wastewater components appear to be controlled by the mass-transfer rate through the surface waters [3]. This transport, or delivery phenomenon can be described by the following expression:

$$N_A = k\,(C_A - C_{AS}) \tag{3}$$

If C_{AS} is assumed to be negligible with respect to C_A, the transport rate of A through water is given by:

$$N_A = k\,C_A \tag{4}$$

This general rate law can represent not only mass transfer, but also any irreversible first-order process, such as a chemical reaction. The assumption of negligible C_{AS} is generally valid when the surface-water concentrations of the component of interest are much higher than the natural background levels in the wetland.

Combining Equation 4 with a material balance for A on the mobile subsystem gives the time-concentration or distance-concentration relationships. For simplicity, water is assumed to be conserved throughout (i.e., no evaporation or rain). For a linear system the downgradient concentration of component A can be given by Equation 5. The same expression also describes the radial variation in concentration for a point discharge system.

$$\ln \frac{C_A}{C_{AO}} = -\frac{kz}{vh} \tag{5}$$

The flow is considered to be steady and continuous, and the depth has been assumed constant. In the linear system, the water velocity can then also be considered constant.

Figure 3 shows the phosphorus profiles obtained from a large-scale experiment over a three-year period. Wastewater was added at a rate of 10,000 m^3/day over a 1000-m line to a 7-km^2 wetland. It can be seen that a zone of saturation expands with time, and that it is followed by a zone of sharply decreasing nutrient concentration. The phosphorus level is seen to approach background values at a decreasing rate. Nitrogen-removal curves exhibit similar behavior [*4*]. This zone of decreasing concentration follows the first-order model proposed in Equation 5, since a plot of field data for ln (C_A/C_{AO}) versus z produces a straight line with a slope $-k/vh$. Figure 4 shows such plots for phosphorus and nitrogen. The linearity of these plots support the hypothesis that nutrient removal is mass transfer-controlled. Similar

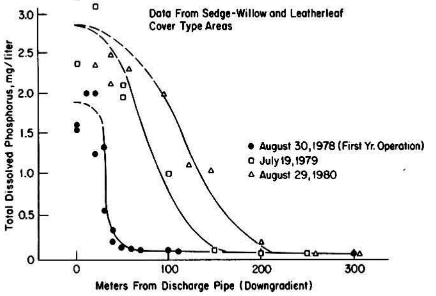

Figure 3. Frontal progression in a linear-flow wetland.

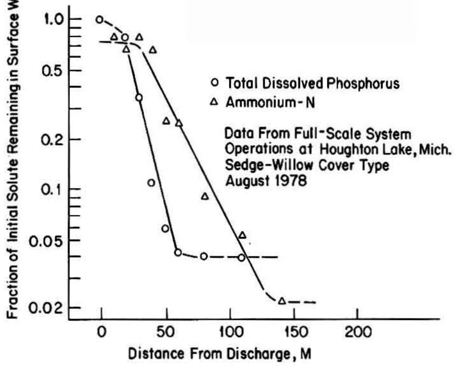

Figure 4. Ion uptake in a linear-flow wetland.

results have been reported for point discharge systems as shown in Figure 5, and also from laboratory studies [3].

Batch operations can be described in an analogous manner, combining Equation 4 with a material balance to obtain the result:

$$\ln \frac{C_A}{C_{AO}} = \frac{-k\,\theta}{h} \qquad (6)$$

Flow systems can also be represented by this equation, identifying θ as the residence time. Batch data [5] for phosphorus removal have been plotted in Figure 6, and they exhibit the same first-order rate dependence observed in flow systems.

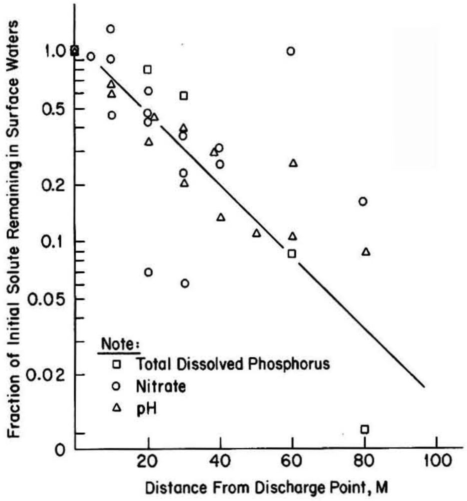

Figure 5. Ion uptake in a point discharge, radial-flow wetland.

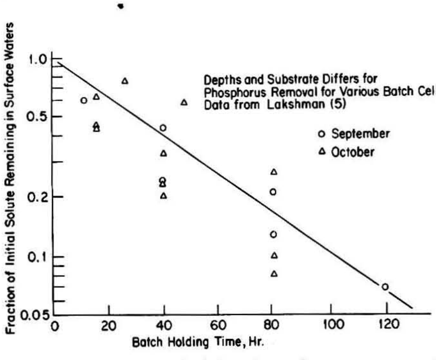

Figure 6. Batch removal of phosphorus from wastewater in constructed wetland cells at Humboldt, Saskatchewan.

Wetland Mass-Transfer Coefficients

Well-established mass-transfer correlations are available for fully developed flow in simple geometries. Such predictive tools might be expected to describe the behavior of nutrient removal in wetland treatment systems, presuming that mass transfer is indeed the controlling rate step. For both laminar and turbulent flow, with developed velocity profiles, the mass-transfer coefficient depends upon the velocity and characteristic dimension of the system (Reynolds number), for short channels, the development of a concentration boundary layer makes the channel length a significant factor.

Bennett and Myers [6] give the following correlation for mass transport, for laminar flow of a fluid over a flat surface:

$$Sh_m = 0.66\,(Re_L)^{1/2}\,Sc^{1/3} \qquad (7)$$

It is convenient to express the mass-transfer coefficient in terms of a depth Reynolds number, $Re_h = \rho v h/\mu$, where h is the surface-water depth. Using a typical solute diffusivity of 1.0×10^{-5} cm²/s and the physical properties of water, Equation 7 can be recast in dimensional form,

for laminar flow:

$$k = 6.6 \times 10^{-5}\,\frac{(Re_h)^{1/2}}{(hL)^{1/2}} \qquad (8)$$

$$k = 6.6 \times 10^{-4}\left(\frac{v}{L}\right)^{1/2} \qquad (9)$$

At higher Reynolds numbers, Re_h greater than about 2000 on a smooth plate, turbulent flow will occur. Mass transport in the turbulent regime for a flat surface has also been described [6]:

for turbulent flow:

$$Sh_m = 0.0365\,(Re_L)^{0.80}\,Sc^{0.43} \qquad (10)$$

Making the same simplifying substitutions as before the dimensional equation is obtained,

$$k = 7.12 \times 10^{-6}\,\frac{(Re_h)^{0.80}}{(L^{0.2}\,h^{0.8})} \qquad (11)$$

$$k = 2.83 \times 10^{-4}\,\frac{v^{0.8}}{L^{0.2}} \qquad (12)$$

Figure 7 shows a plot of Equations 9 and 12 for typical conditions encountered in a wetland with primarily sedge and

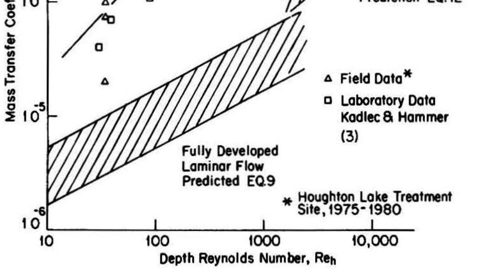

Figure 7. Mass-transfer coefficients—predicted and measured.

willow vegetation. Natural channelization has been assumed to occur, with open water runs varying from approximately one to ten meters long. Water depth has been assumed to be on the order of 15 cm. The values predicted by these correlations fall within the bands indicated.

Experimental results are also shown on Figure 7. The mass-transfer coefficients are higher than predicted by the generalized correlations. This feature can be explained by consideration of "entrance effects". Most often, the nature of channelization and the flow rates of surface water in the wetland do not result in fully developed velocity profiles. Average transport rates are therefore higher, due to the reduced resistance resulting from the absence of a complete momentum boundary layer.

The experimental data for the mass-transfer coefficient at the Houghton Lake site might be represented by

$$k = a\,\mathrm{Re}_h \tag{13}$$

If a hydrological model of overland flow at this site is assumed to be of the form (constant gradient):

$$v = b\,h^2 \tag{14}$$

then the velocity dependence of the mass-transfer coefficient can be determined:

$$k = cv^{3/2} \tag{15}$$

A plot of the experimental mass-transfer data versus water velocity is shown in Figure 8. A line with slope 3/2, corresponding to Equation 15, has been drawn through these data. Other hydrology models will result in other slopes on this plot.

TRANSPORT AND REMOVAL OF SUSPENDED SOLIDS

The suspended-solids content of wastewater or of surface water is in itself an important water-quality parameter. The movement of suspended solids in a wetland system also constitutes a mechanism for transport of phosphorus, nitrogen, and other substances. The importance and nature of such solids in wetland wastewater-treatment systems has been largely unidentified.

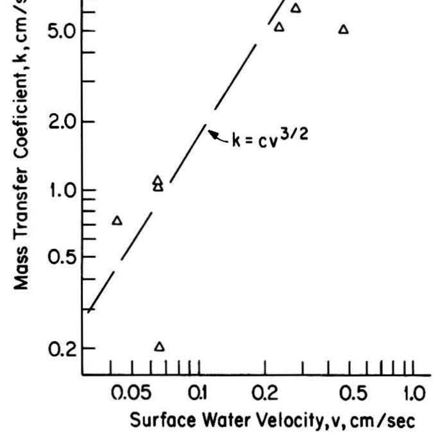

Figure 8. Effect of velocity on the mass-transfer coefficient. Data from Houghton Lake, Michigan, treatment site.

Suspended solids found in wetland surface waters may come from varied sources: incoming wastewater, stream-borne silt and inorganics, detritus from algae and vascular plants, and, in the literal sense, as mobile organisms, particularly invertebrates. Slow surface-water velocities and long residence times promote the retention of solids. Vegetation causes surface waters to follow a tortuous path, around and through innumerable obstacles which provide sites where suspended particles may impact, lose momentum, and settle.

The suspended material in a wetland may be but a small fraction of the accumulated "suspendable" pool. Preliminary measurements at the Houghton Lake treatment site indicate that this potential pool represents on the order of several grams of solids per liter of surface water, and these solids possess a relatively high nitrogen and phosphorus content [7]. Some of these solids are of nearly neutral buoyancy, exhibiting re-suspension in a still-water column due to temperature induced density changes. It is not known how mobile these suspendable sediments are under varied hydrological conditions, and seasonal effects have not been elucidated.

The re-suspension of sediments has received considerable attention in the literature [*8*], [9], [*10*], but studies are generally confined to beds of non-cohesive granular solids. Shields [*11*] defined a dimensionless stress, by forming a ratio between the shear stress applied to the sediment bed, τ, and the weight of the top layer of submerged solid grains per unit area,

$$S = \frac{\tau}{(\rho_s - \rho_w)gD} \tag{16}$$

The critical value of the dimensionless shear stress is the point of incipient re-suspension. Shields further argued that this critical value could be correlated as a function of the boundary Reynolds number alone, based on dimensional considerations. The boundary Reynolds number is defined as

$$\mathrm{Re}_B = \left(\frac{\tau}{\rho_w}\right)^{1/2} \frac{D}{\nu_w} \tag{17}$$

Settling times for solids in freshwater wetlands are measured in minutes or hours, based on our data. Re-suspension is roughly proportional to velocity, as shown in Figure 9.

SORPTION: THE FIRST UPTAKE PROCESS

Mass transfer will be limiting if the uptake processes are faster, and have a reasonable capacity. We shall therefore examine some typical information.

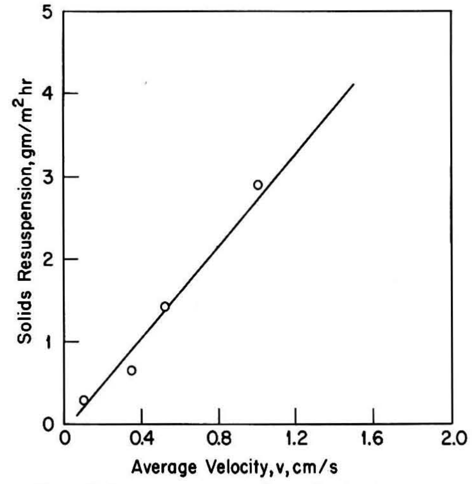

Figure 9. Re-suspension rates for wetland sediments.

Phosphorus

The rapid immobilization of phosphorus from wastewater by organic soils has been reported by many investigators [*12*], [*13*], [*14*], [*15*]. The process has been shown to reach saturation very rapidly, as shown in Figure 10, and the uptake is at least partially reversible [*12*]. The phenomena is well-described by a Freundlich-type isotherm for equilibrium adsorption,

$$\log C_S = a \log C_A + b \qquad (18)$$

Equilibrium data for typical wetland soils are presented in Figure 11. The inorganic phosphorus capacity of a particular soil will be determined by many factors. Adsorption is considered to be limited in part by iron, aluminum, and other inorganic components to provide the means for phosphorus fixation [*16*], [*17*], [*18*], [*19*]. The sorption capacity of organic soils can also be reduced by the presence of inactive inorganic diluents such as sand [*20*].

Phosphorus profiles in surface water at the Houghton Lake treatment site (Figure 3) show the progression of a saturation front; this behavior is consistent with the concept of equilibrium adsorption.

Nitrogen

The tendency of other wastewater components to adsorb on wetland soils has not been so clearly quantified. Nitrogen compounds undergo a complex set of transformations via biological and chemical reactions. These processes can occur at rates which are rapid enough to hamper experimental attempts to obtain reliable equilibrium adsorption data.

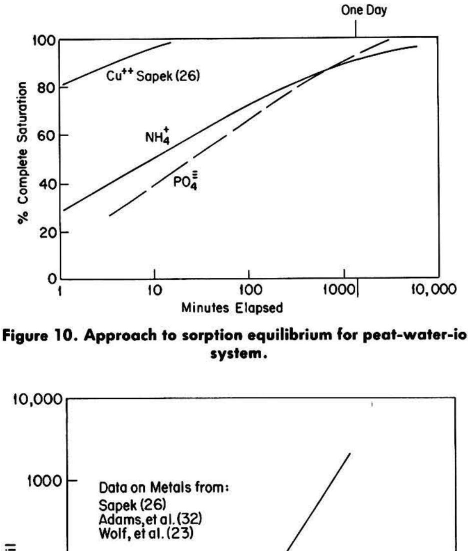

Figure 10. Approach to sorption equilibrium for peat-water-ion system.

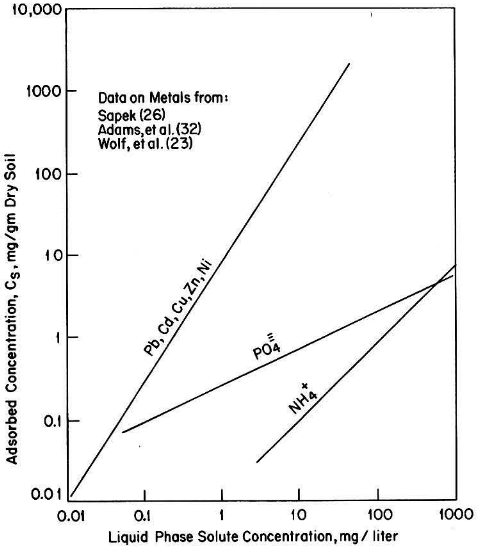

Figure 11. Equilibria for peat-water-ion systems.

Studies have been undertaken in the laboratory, to assess the adsorption capacity of some peat soils for inorganic nitrogen compounds [*21*]. Microbial processes, in particular, make experimental results more difficult to interpret, and sterilization techniques have been shown to modify the soil's adsorption characteristics. Figure 11 shows equilibrium data for the adsorption of ammonium ion. Although data are sparse, and do not fit the model proposed in Equation 18 as well as phosphate, the behavior may still be approximated by a Freundlich-type model. Uptake of ammonium ion was rapid in these experiments, with sorption largely complete in less than one day (for dilute solutions). Alternatively, in the case of nitrate ion, no appreciative sorption on peat was observed. Chloride is likewise not adsorbed by organic soils.

Heavy Metals

Many investigators have reported that heavy metals are often closely associated with sediments and upper-soil horizons [22], [23], [*24*], [25]. Actual measurements of equilibrium uptakes in wetlands are difficult to obtain. Literature data consists almost entirely of specific compartmental assays at a single point in time and offer very little information on potential removal rates or sorption equilibria. Metal concentrations in applied wastewater are usually quite low, typically below the detection limits of routine analytical work. A strong affinity for heavy-metal sorption would imply that soils could rapidly remove them from overlying waters. Sorption of cupric ion on peat-muck soils has been studied by Sapek [*26*]. Typical uptake data are shown in Figure 10.

Equilibrium sorption data as available from several sources are shown in Figure 11. These high soil capacities suggest that wetlands can remove heavy metals from wastewater very effectively. Removal rates are likely to be limited only by mass transfer from surface waters to the soil. Soil capacity for heavy metals has been observed to increase with organic content [22], [*27*] and pH and redox potential have also been shown to play a role [*28*], [*29*], [*30*], [*31*].

CONCLUSIONS

In summary, the factors which control the rate and extent of ion sorption on peat and other wetland soils have not been fully elucidated. Rates are fast in comparison to typical biological processes, thus suggesting a rapid capture mechanism such as adsorption, which can make nutrients more readily available to the organisms present. The presence of these fast sorption mechanisms results in the observed first-order removal rates in wetland systems. Information is lacking on the temperature dependence of adsorption rates, and it is conceivable that during winter operation the sorption step may provide a significant resistance to nutrient removal. Operating experience with wetland treatment systems has revealed an apparent nutrient saturation phenomenon in the vicinity of wastewater introduction; this behavior is consistent with an approach to an adsorption equilibrium. The rate of nutrient removal in unsaturated zones may be limited only by mass transfer.

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Treatment of Heavy Metals in Wastewaters

What wastewater-treatment method is most cost-effective for electroplating and finishing operations? Here are the alternatives.

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The Federal Government has allowed the General Pretreatment Regulations to take effect as of January 31, 1982 (46 *Federal Register* 4518). In addition, regulations for the electroplating industry have been reissued in the January 13, 1982 *Federal Register* with a compliance date of January 28, 1984. These regulations include maximum discharge criteria for heavy metals. These limitations closely parallel the present criteria promulgated for the plating/surface-finishing industry. The heavy-metals limitations can be broken down into two basic classifications — discharges less than 10,000 gallons per day, and those discharges greater than 10,000 gallons per day to Publicly Owned Treatment Works (POTW). There are complicated formulas for removal credits, but most platers will probably opt to comply with one of the two discharge schedules below (Table 1 and Table 2).

This paper will present a discussion of alternative methods used to treat the typical heavy-metal wastewaters most often generated by electro-plating and surface-finishing operations. Before considering any form of wastewater treatment, it is essential that the manufacturer review and reduce his water usage wherever feasible. This can be done with rinse-tank controllers (conductivity), counterflow rinsing, flow restrictors, and foot pedals. Water-usage reductions will permit the manufacturer to reduce the volume of wastewater generated and thus reduce the capital cost of the wastewater-treatment system.

TABLE 1

LIMITATIONS FOR DISCHARGES MORE THAN 10,000 GALLONS PER DAY TO POTW

Pollutant	Maximum Per Day (mg/l)	Maximum for 4 Consecutive Days (mg/l)
Cadmium	1.2	0.7
Chromium^T	7.0	4.0
Copper	4.5	2.7
Cyanide^T	1.9	1.0
Gold	1.2	0.7
Lead	0.6	0.4
Nickel	4.1	2.6
Zinc	4.2	2.6
Total Metals	10.5	6.8

After water-saving steps have been taken, flow studies and analyses of the waste streams must be conducted. With this basic information, wastewater treatment equipment can be selected and sized. Batch treatment can be used where flows are small, irregular, or where the strength of the waste may be quite high or extremely variable [*1*]. A typical batch-treatment system is shown in Figure 1. Batch systems are available in various modes, ranging from completely manual to fully automatic with a programmable controller. With a batch-treatment system, all treatment operations can be performed in one vessel, depending upon the presence of cyanide/chrome-bearing wastes. Continuous systems require the use of separate integral reaction units for each treatment reaction.

Any wastewaters which contain high amounts of oils must first pass through some type of oil-separation equipment. Floating oils can be skimmed mechanically, while emulsified oils can be forced to separate either with chemical aids, a coalescer, or with ultrafiltration. If BOD/COD is present in excess of the discharge criteria, either aeration or carbon adsorption must be used to reduce the BOD/COD to dischargeable levels [*2*].

ORIGIN OF WASTES

Cyanide-bearing wastes generally originate from cyanide-bearing cleaners, cyanide dips, and plating solutions for the following metals: copper, zinc, cadmium, brass, bronze, silver, and gold. Both concentrated and dilute wastes are possible. Concentrated wastes are the result of discarding spent solutions. Dilute wastewaters are the result of dragout or carry-over from a process solution which is rinsed off the part. The two should be treated together with the concentrated cyanide wastes bled into the dilute stream. Cyanide waste streams should be segregated from other wastes for treatment.

TABLE 2

LIMITATIONS FOR DISCHARGES LESS THAN 10,000 GALLONS PER DAY TO POTW

Pollutant	Maximum per Day (mg/l)	Average of Daily Values For Four Consecutive Monitoring Days Not to Exceed (mg/l)
CN, Amenable	5.0	2.7
Cd	1.2	0.7
Pb	0.6	0.4

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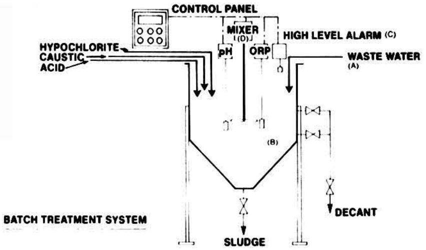

Figure 1. Typical batch-treatment system.

Chromate-bearing wastes originate from plating, bright dip, conversion coating, and anodizing. Again, wastes may be dilute or concentrated. Dilute wastes result from drag-out or carry-over from the process solution, which is removed from the work-piece, while concentrated streams result from the periodic dumping of spent baths or solutions. The two streams should be treated together with the concentrated chromate stream being bled into the dilute stream. Chromate streams must be segregated from other wastes for treatment.

Acid/alkali wastes make up the balance of the wastewater stream from most platers/finishers. The acids are generated from acid cleaners or pickling solutions, bright dips, acid dips, and their subsequent rinses. Alkalies result from alkaline degreasing and cleaning solutions and their subsequent rinses. The acid/alkali wastes, the cyanide-bearing wastes, the chromate-bearing wastes, nickel, copper, and zinc acid plating baths/rinses all contain heavy metals.

CONVENTIONAL TREATMENT

The most common method of treatment of cyanide wastes is alkaline chlorination. The chlorine may be added directly as chlorine gas, or in the form of sodium hypochlorite solution. The complete destruction of cyanide, i.e., conversion to carbon dioxide and nitrogen is a two-step oxidation process. The chemical reactions for the process with sodium hypochlorite appear in Figure 2.

When chlorine gas is used, sodium hydroxide must be added in the initial reaction to form sodium hypochlorite. Oxidation of the cyanides then proceeds by the same mechanism. Both stages of the reaction are pH-dependent. With the first stage, the reaction rate decreases as the pH decreases. In the second stage, the reaction rate increases as the pH decreases. It is, however, very important to note that, in the second stage, pH's below 7 must be avoided since at these low pH's cyanate will convert to ammonia.

The use of ozone as an oxidizing agent for cyanides is growing in popularity. The oxidation process occurs at ambient temperatures and can easily be automated. The major disadvantage is that ozone must be generated on-site and is relatively expensive. In addition, oxidation beyond the cyanate level is limited.

1st Stage

NaOCl (Sodium Hypochlorite) + NaCN (Sodium Cyanide) ⟵ (pH 10.5)

NaCNO (Sodium Cyanate) + NaCl (Sodium Chloride)

2nd Stage

$\mathrm{2NaCNO}$ (Sodium Cyanate) + NaOCl (Sodium Hypochlorite) + $\mathrm{H_2O}$ (Water) ⟵ (pH 8)

$\mathrm{2CO_2}$ (Carbon Dioxide) + $\mathrm{N_2}$ (Nitrogen) + $\mathrm{3NaCl}$ (Sodium Chloride) + NaOH (Sodium Hydroxide)

Figure 2. Cyanide oxidation.

The chromate-bearing wastes must first undergo reduction from the hexavalent state to the trivalent state. This can be accomplished with various reducing agents, the most common being sodium metabisulfite, ferrous sulfate, and sulfur dioxide. The reaction of sodium metabisulfite with chromate is shown in Figure 3.

The oxidation-reduction potential can be used to plot the course of the reduction reaction for chromate and the oxidation reaction for cyanide. Thus, an ORP meter/controller is an essential component, along with a pH meter/controller to assure proper treatment of cyanide and hexavalent chrome. Once they have been treated they can be combined with the general acid/alkali wastes for subsequent pH adjustment and the precipitation of heavy metals.

Single-stage continuous neutralizers are usually suitable for electro-plating wastes, using acids, sodium hydroxide, or lime. If the wastewater is subject to rapid pH variations or flow variations, a two-stage system should be used [*1*]. The retention time in each vessel is typically ten minutes. The term "neutralizer" is a misnomer today, because of the treatment to a specific pH for optimum heavy-metals removal. Metals precipitate at various levels of pH, depending on various factors such as: the metal itself, the insoluble salt that has been formed (e.g., hydroxide, sulfide, etc.), the presence of complexing agents such as EDTA (ethylene diamene tetraacetic acid), ammonia, acetic acids, etc. [*3*]. Theoretical curves for the precipitation of various metals as hydroxides are shown in Figure 4.

When two or more heavy metals are present in the same waste stream, the optimum pH for precipitation may be different than the optimum pH for one particular ion. In order to determine the optimum treatment process, a bench-scale laboratory testing program should be conducted and should include the use of various chemicals and various pH ranges to determine their effect in producing the best effluent. Various polymers should also be tested for their use in improving the settleability of the metal precipitates. Polymer is typically added immediately after pH adjustment in a flocculation vessel. The flocculated wastewater is then permitted to settle.

Various types of settling vessels are available. They include conventional center feed-peripheral discharge circu-

$\mathrm{3NaHSO_3}$ (Sodium bisulfite) + $\mathrm{2H_2CrO_4}$ (Chromic Acid) + $\mathrm{3H_2SO_4}$ (Sulfuric Acid) ⟵ (pH 2.0)

$\mathrm{Cr_2(SO_4)_3}$ (Chromic sulfate) + $\mathrm{5H_2O}$ (Water) + $\mathrm{3NaHSO_4}$ (Sodium bisulfate)

Figure 3. Chromate reduction.

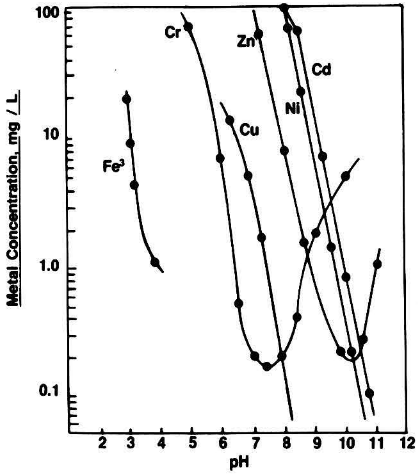

Figure 4. Precipitation of heavy metals as hydroxides.

lar clarifiers, rectangular conventional clarifiers, slant-tube clarifiers and lamella-type clarifiers. The slant-tube and lamella-type clarifiers offer improved settling while occupying less area than conventional clarifiers. The precipitated sludge from the clarifier is removed at 1-2% solids for further thickening in a sludge thickener and/or subsequent dewatering.

The clarifier overflow may contain residual suspended solids requiring removal with a polishing filter. This ensures maximum removal of metals. A dual-media gravity filter or pressure filter is the most prevalent choice for filtration. When the filter reaches terminal head loss, it must be backwashed, which takes 15-20 minutes. During this time, it is out of service, with the main sump (feeding the pH-adjustment unit) holding the incoming flow. One alternate to this is to use a duplex filtration system assuring continuous operation. Effluent polishing can also be provided continuously with the DynaSand™ Filter which is a continuous-backwashing, upflow, deep-bed granular-media filter. The feed is introduced into the bottom of the unit and flows upward through a series of riser tubes and is then evenly distributed through the distribution hood. The influent flows upward counter to the downward-moving sand bed; the filtered effluent then exists *via* an overflow weir. The sand bed and the accumulated solids are drawn downward into the suction of an airlift pipe at the center of the filter which transfers the slurry upward through the center of the unit. The scouring action frees the solids and they are then separated in the washer/separator which returns the sand to the filter and the solids to the reject stream. This device permits continuous backwashing utilizing 2-3% of the flow. The filtered, treated wastewater is then discharged to the POTW.

After the sludge has been collected from the clarifier, it is pumped to a sludge-thickening device. Usually, a conical-bottom tank is used with decant connections located on the side of the tank. This enables the initial collected sludge to be concentrated from 1-2% solids by weight to a final concentration of 4-8% solids by weight. Thickening improves the performance and efficiency of the final dewatering process and results in substantial volume reductions to reduce both the disposal and handling costs. From the sludge-thickening tank the sludge can be further dewatered with the use of a centrifuge, vacuum filter, or a plate-and-frame filter press.

A vacuum filter can work either continuously or as a batch operation. The common type of vaccum filter is the rotary-drum vacuum filter. This unit has three basic zones of operation: 1) slurry pick-up, 2) cake-drying area, 3) scraper/discharge. The system is constructed as a cylinder with various types of filter media. The cylinder is usually submerged about 40% with the speed of rotation set to obtain optimum pick-up, dewatering, and cake removal with the filtrate returned to the main process sump for retreatment. The dewatered cake contains from 20-30% solids [*4*].

The filter press is one of the most common devices utilized for the dewatering of metal-hydroxide sludges. The system consists of a frame to support the plates. Plates can be either of the gasketed or non-gasketed type. Typically, the press is opened or closed with either a hydraulic system or a hand crank. The hydraulic system reduces the manual cranking labor. Once the press has been closed, the sludge is pumped to the press, where it disperses to each chamber simultaneously. Under pressure, the solids deposit uniformly on the surface of the cloth with the initial build-up acting as a filter. In most applications, the cake will build up to completely fill the chamber in about a two-hour period with the pump "stalling-out" when the chambers are full. The pump is then turned off and air is blown into one of the discharge ports of the press to remove any excess water and to separate the cake from the filter media. The press is then opened and the dewatered cake removed from the unit. The press typically produces sludge containing 20-40% solids by weight, while requiring only minimal manual labor.

In applications where the volume of sludge to be dewatered is large, the use of a centrifuge is very economical. The slurry is fed to the center of the unit, where it is accelerated with the rotational speed of the unit and packs on the outside bowl of the unit with the clear liquid collected through a filter screen. The heavier solids are forced towards the sludge discharge where they are typically removed by a screw conveyor. The concentrate is returned to the main process sump for reprocessing. Centrifuges can produce dewatered cakes of 15-25% solids by weight.

Bag filters are also used on occasion to dewater sludge. Some units utilize a series of open filter bags, while others utilize pumps to feed bags in a central housing. The bags can produce cakes ranging from 6-12% solids by weight. Once the sludge has been dewatered, it must be disposed of and this requirement is often the major factor in selecting a more effective dewatering process.

SULFIDE PRECIPITATION

Sulfide precipitation can be more practical than hydroxide precipitation in removing chromium because it directly reduces the hexavalent chrome to its trivalent state, eliminating the need for intermediate pH control. Sulfide precipitation is accomplished with either the soluble-sulfide or insoluble-sulfide process. With the insoluble process, an excess of ferrous sulfide is added, enabling the iron to give up its sulfide and to precipitate any metal with a lower solubility than the ferrous sulfide. With alkaline pH, the iron precipitates in the hydroxide form. In the soluble-sulfide process, a sulfide-ion probe is utilized to measure/control the addition of soluble sulfides such as sodium sulfide or sodium hydrosulfide. The soluble-sulfide system typically requires a higher chemical demand and produces a larger volume of sludge than hydroxide precipitation. Sulfide precipitation is relatively insensitive to the presence of most chelating agents and performs well on many complexed heavy metals [2]. But sludge disposal can present a problem with no adequate data available to confirm the existence of sulfide sludges with long-term stability and it therefore may be difficult to obtain regulatory agency approval to dispose of the sludge in some areas [5].

ELECTROCHEMICAL REDUCTION

Chromium reduction is the most common application for electrochemical reduction/precipitation. This process utilizes consumable iron electrodes and electricity to generate ferrous ions, which react with the hexavalent chrome to produce trivalent chrome. Because of the introduction of ferrous ions into the waste stream, some additional solids will be generated. Maintenance includes biweekly replacement of electrodes and washing of electrodes (10-15 minutes/day). The conventional chemical reduction system has a combined treatment and sludge-disposal cost advantage over the electrochemical method when the influent Cr^{+6} exceeds 5 ppm [2].

INTEGRATED WASTEWATER TREATMENT

The integrated-system approach incorporates the waste-treatment step as part of the actual plating operation. In this type of system, the drag-out on the work-piece is treated in a rinse tank that contains the treatment chemical. For example, immediately following the chromic-acid bath there would be a chromic-acid waste-treatment rinse. This rinse would be in a closed loop with a chromium waste-treatment reservoir which is continually dosed with the required make-up sodium bisulfite, or other reducing agent. Following the treatment rinse, there would be a water rinse tank which would discharge to the conventional waste-treatment system for pH adjustment and removal of any heavy metals; however, the chrome would now be in the trivalent stage. A similar approach is utilized following the cyanide baths.

INSOLUBLE STARCH XANTHATE

Insoluble starch xanthate (ISX) is a recent process developed by the U.S. Department of Agriculture to remove heavy metals from wastewater. ISX is made from commercial crosslinked starch by reacting the starch with sodium hydroxide and sodium disulfide. To give the product additional stability and improve the settling rate, magnesium sulfate is added. ISX acts as an ion-exchange material, exchanging the heavy-metal ions and replacing them with manganese and sodium ions. The process generates a significant amount of sludge, although the sludge does settle rapidly and can be dewatered to 30-90% solids by weight. This sludge is very stable with no leachate problems evident. ISX is very effective in the treatment of complexed copper but can also be used with most heavy metals.

ELECTROLYTIC TECHNIQUES

Electrolytic techniques have recently been utilized to plate out dissolved metals, reduce chromium, and to oxidize cyanide from wastewater. The major operating cost is the electrical current, with no chemical treatment required. The high electrical resistance of dilute solutions has made only more concentrated rinses economically treatable until very recently. Two companies are presently actively marketing electrolytic-treatment systems.

EVAPORATION

The evaporation process has been utilized successfully on virtually all types of plating baths. One of the most important benefits of the evaporative recovery system is that it enables the return of drag-out wastes of higher concentrations than the original bath. In those installations, where the evaporation losses are minimal, and where the drag-in is equal to the drag-out, there is considerable merit in the use of evaporative recovery. There are basically three types of evaporators: vacuum evaporators, thin-film evaporators, and atmospheric evaporators.

Vacuum evaporators utilize reduced pressure to lower the boiling point of the solution, therefore allowing a lower rate of decomposition of cyanide solutions. This also reduces both the carbon-dioxide adsorption and the air entrainment of the solution being boiled.

The thin-film or rising-film evaporators are designed to provide a very fast rate of heat input to a thin film of solution. This minimizes both crystallization and solids precipitation on the heat-exchanger surfaces, resulting in lower maintenance requirements and better efficiency in the heat transfer. The thin-film and rising-film evaporators can be combined with vacuum evaporation to take advantage of the benefits of both processes, inhibiting any thermal degradation of the solution additives and reducing energy consumption.

Atmospheric evaporators are normally operated below the boiling temperatures. The evaporator column is designed similarly to an exhaust scrubber, with a vent fan passing a large volume of air through a packed column where the warm solution is sprayed from the top. The exhaust air is saturated with water. The atmospheric evaporators are very cost-effective with chromic acid, when used in conjunction with the scrubbing of the plating-tank exhaust.

The savings and economics for evaporation are dependent on the concentration of rinse water being evaporated and the volume of drag-out. Chromic-acid plating solutions do contain contaminants which, when evaporated and returned to the bath, can result in bath failure. The use of a cation exchanger before the wastes are concentrated in an evaporator is therefore recommended [7].

REVERSE OSMOSIS

The name "reverse osmosis" was originally derived because it is the transport of water in a reverse direction of normal osmosis, where water flows from a less concentrated solution through a semi-permeable membrane to a more concentrated solution. The feed solution flows over the surface of the membrane. The membrane is typically a cellulose acetate film very similar to heavy cellophane. Pressure is utilized to force a percentage of the water in the solution through the membrane while a little of the initial water, enriched in solutes, remains to be transported away. The solution entering the membrane is designated as the feed, while the material forced through the membrane is called the permeate. The enriched solute water is referred to as the concentrate or reject stream.

The major difficulty with reverse osmosis (RO) Systems is the problem of maintaining membrane performance. The pH must be maintained in a pH range of 2.5 to 11 to ensure reasonable membrane life. Good filtration should always be utilized to protect the membrane surface from fouling. Reverse osmosis has great potential for the recovery of raw metal materials in the metal-finishing rinses after plating. At present, systems have been utilized on chrome, nickel, and copper plating-line rinses, producing as the by-product pure water for re-use.

ION EXCHANGE

Ion exchange is a reversible chemical reaction, where an ion from the solution is exchanged for a similarly charged ion attached to a solid particle. Typically, synthetic organic resins are utilized because of their superior capabilities of being manufactured for specific applications. The organic resin is composed of polyelectrolytes with a high molecular weight, which can exchange their mobile ions with those of a similar charge in the surrounding medium. Ion exchange is ideally suited for dilute solutions, with the treated water being of very high purity. Although every known metal has been recovered, separated, and purified by some ion-exchange process in the laboratory, on a commercial scale only a few are treated with ion exchange [9]. Economics plays the major role in determining whether it is feasible to treat with ion exchange.

There are various types of resins, but the two basic classifications are cationic and anionic. The cationic resins have positively charged mobile ions available for exchange, while the anionic have negatively charged mobile ions available for exchange. Both of these groups can be further classified as strong- or weak-base anion exchangers, or strong- or weak-acid cation exchangers, and are so named because of their chemical behavior. Most industrial applications utilize columns with fixed beds of ion-exchange resin. Once the resin has become exhausted, the system must be regenerated. A cationic resin is regenerated with acid, which ellutes the collected positively charged ions and replaces them with H^+ ions followed by a slow water rinse to remove any residual acid. An anionic resin is regenerated with caustic which ellutes the collected negatively charged ions and replaces them with $OH-$ ions.

Ion exchange is used in the metals and plating industries to remove trace pollutants from wastewater after a conventional system or to recover bath-solution drag-out from rinse water and to return the purified water for re-use. One example is the use of ion exchange to recover and return chromic acid to the bath. The rinses are first collected in a holding tank, where they are pumped at a constant rate through a sand filter and an activated-carbon filter. Four columns are utilized, two anion columns and two cation columns. The flow is first pumped to the cation column and then through two anion columns. The cation column is utilized to remove any heavy-metal contaminants while the anion columns remove the hexavalent chromium from the rinse water. When the first anion column has been ex-

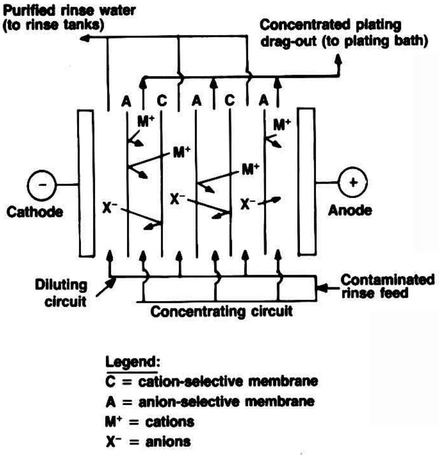

Figure 5. Electrodialysis unit flow schematic.

hausted, it is removed from operation and regenerated with caustic and returned on-line as the second column. The caustic regenerant stream is now sodium chromate and is passed to the second cationic column. The sodium ions are exchanged for hydrogen ions, producing chromic acid and water, and can be returned to the bath. When the cationic columns are exhausted, they must be regenerated with caustic, with the regenerant treated for removal of heavy metals and pH adjustment.

The major disadvantage of the ion-exchange system is the need to be regenerated after exhaustion. This produces a concentrated waste stream which has to either be treated or hauled away for disposal.

ELECTRODIALYSIS

Electrodialysis is used to concentrate or separate ionic species in a water solution. A water solution is passed through alternately placed anionic and cationic permeable membranes with an electric potential applied across the membranes. The electric potential provides the force to enable ion migration. Therefore, there are two hydraulic circuits, one which is ion-depleted while the other is ion-concentrated. The electrical potential across the membrane determines the degree of purification/concentration needed to return the plating chemicals to the bath [2].

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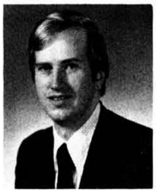

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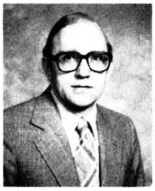

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Fate of Specific Pollutants During Wet Oxidation and Ozonation

Where do the pollutants wind up in oxidational purification processes? Here is a well documented experimental study.

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Wet oxidation and ozonation are similar in that both processes accomplish oxidation of organic matter in aqueous solution. Whereas ozonation relies on the oxidation potential of dissolved ozone at ambient temperatures and pressures, the wet-oxidation process employs an excursion in temperature and pressure to establish favorable conditions for dissolved oxygen to react. Typical conditions for wet oxidation range from 200°C and 4 MPa to 315°C and 15 MPa. Both processes have application in the removal of specific organic substances from aqueous waste streams. Ozonation would be expected to offer economic advantages over wet oxidation for more dilute wastes. As the concentration of oxidizable organic matter increases to roughly 4%, the wet-oxidation process becomes thermally autogenous and further increases in concentration of oxidizable organic matter can lead to energy recovery.

Additional similarities between the processes are that each involves interphase mass transfer of oxidant from the gas to the liquid state and the rate of each may be limited by the rate of mass transfer. Furthermore, each process has been reported to produce a residual of low-molecular weight organic acids which are oxidized only slowly. Finally, it has been hypothesized by various investigators that hydroxyl radicals play an important role in the reactions of each process.

The purpose of the research reported in this paper is to assess the ability of wet oxidation and ozonation to destroy five typical priority pollutants (phenol, 2-chlorophenol, 1,2-dichloroethane, 4-nitrophenol, and dimethylphthalate). Particular attention has been paid to interpreting the batch kinetic data, exploring the influence of initial pH on ozonation and identifying and measuring the low-molecular weight organic acids produced.

BACKGROUND

Reactions and Products

Rice and Browning [1,2] have compiled an extensive literature review of the reactions occurring and products produced during ozonation of various classes of organic compounds. It has been reported that ozone reacts with aromatic compounds to produce catechol and hydroquinone followed in turn by muconic, maleic, glyoxylic, glycolic, oxalic, and formic acids. The corresponding aldehydes have frequently been detected as precursors of these acids. Because the lower-molecular weight acids generally react more slowly than their parent compounds, the rate of total organic carbon removal decreases with time. Although it has been reported that formic acid is readily converted to CO_2 by ozone, Japanese workers [3] have recently observed formic acid to be the major organic product produced during ozonation of phenol.

In contrast to ozonation, significantly less research has been reported on the reaction products produced during wet oxidation of specific substances. Knopp *et al.* [4] indicate the major intermediate and end products of wet oxidation to be primarily low-molecular weight acids (acetic, formic) with lesser amounts of low molecular weight aldehydes. Acetic acid has been reported to be a major end product produced during wet oxidation of phenol, 2-chlorophenol [5], and propionic acid [6].

Various investigators have hypothesized hydroxyl radicals to play an important role in the reactions of wet oxidation [7,8] and ozonation [9]. In view of this, one might expect similarities between the reaction products produced by each process.

Ozonation Kinetics

The kinetics of the ozonation reaction have been expressed as [9,10]:

$$r = k_o C(O_3) \qquad (1)$$

where

r = rate of reaction of organic per unit volume, mol L^{-3} t^{-1}
k_o = reaction rate constant, L^3 mol^{-1} t^{-1}
C = aqueous concentration of organic reactant, mol L^{-3}
O_3 = aqueous concentration of ozone, mol L^{-3}

For phenol, the reaction-rate constant has been shown to increase with pH. A reasonable explanation is that, as pH increases above 3, ozone decomposes to form highly reactive hydroxyl radicals and phenol ionizes to form the more reactive phenolate ion (pK = 9.9). Hoigné and Bader [9] have proposed a reaction scheme in which ozone itself reacts directly and selectively with specific organics at low pH values. At higher pH values, the reaction is less selective and is accomplished by the decomposition products of ozone such as hydroxyl radicals. The following values have been given for ozonation rate constants [10]:

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phenol - 400 ℓ/(mol·sec) (20°C, low pH, direct reaction)
2-chlorophenol - 200 ℓ/(mol·sec) (20°C, low pH, direct reaction)
phenolate ion - 1.3×10^7 ℓ/(mol·sec)

Gurol [10] recently studied the kinetics of ozone decomposition and reaction with phenol and developed a mathematical model to predict the profiles of phenol, muconic acid, hydroquinone, and catechol during semi-batch ozonation experiments at pH 3. At higher pH values, the model failed to describe the observed profiles, presumably because the reaction rates were increased to the point where a significant amount of ozone reacted in the film and enhanced the mass-transfer rate.

Others [11,12] have described the phenol profile during semi-batch ozonation by:

$$\frac{dC}{dt} = K_cFC \tag{2}$$

where

K_c = combined rate constant, mol phenol $(\text{mol } O_3)^{-1}$
F = dosage rate, moles of ozone per minute per mole phenol initially present, mol $\text{mol}^{-1}\ t^{-1}$

This expression combines the effects of mass transfer and reaction and, because of this, the combined rate constant, K_c, is system-specific.

Wet-Oxidation Kinetics

Many of the literature reports on wet oxidation do not lend themselves to kinetic interpretation because they are concerned with heterogeneous mixtures such as sludge or are based on nonspecific measures such as chemical oxygen demand. However, a few studies on pure substances have been reported.

Pruden and Le [13] expressed the kinetic rate equation for wet oxidation of phenol as:

$$r = k_w\ C(O_2) \tag{3}$$

where r and C are as defined above,

k_w = wet oxidation reaction rate constant, $L^3\ \text{mol}^{-1}\ t^{-1}$
O_2 = aqueous concentration of oxygen, mol L^{-3}

These workers evaluated O_2 in terms of K_La and Henry's constant to develop a flow reactor model which was supported by their data. Ploos van Amstel [14] studied wet oxidation of glucose and, based on an apparent half-order dependence of the reaction rate on glucose concentration, concluded that the reaction took place in the diffusive film and was mass-transfer-limited. Recently, Skaates *et al.* [15] pointed out that this half-order dependence is in accordance with a reaction following the kinetics of Equation 3, taking place with the diffusive film.

EXPERIMENTAL

Ozonation

The ozonation reactor consisted of a glass tube 2.54 cm in diameter with a liquid depth of 50 cm and a total height of 61 cm. Ozone was fed through a single 1.6-mm orifice at the bottom. During typical experiments, 250 ml of aqueous solution at 25°C and initial reactant concentration of 50 mg/ℓ or 1000 mg/ℓ was contacted with 0.6 ℓ/min of ozonated air produced by a Welsbach T-816 ozonator. The ozone concentration in the feed gas averaged 25 mg/ℓ and the mass rate of ozone fed to the reactor averaged 15.6 mg/min. Ozone in the feed and exit gas was determined by passing these streams through 2% KI traps followed by a wet test meter. During several experiments, the KI traps were alternated at 2-minute intervals so that ozone consumption could be measured as a function of time. Figure 1 shows a diagram of the ozonation system.

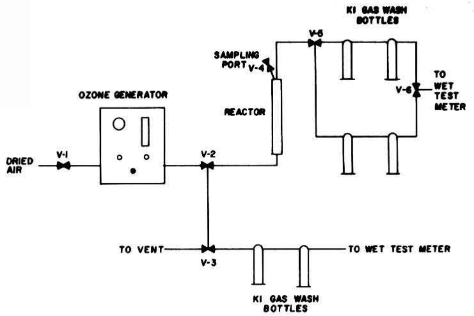

Figure 1. Schematic Diagram of experimental ozonation system.

Initial pH values of 10 and 6 were obtained by dissolving the organic reactant in the following phosphate buffer solutions:

pH 10: 0.05 $\underline{M}$ Na_2HPO_4, 1.5×10^{-3} $\underline{M}$ NaOH
pH 6 : 0.1 $\underline{M}$ KH_2PO_4, 1.1×10^{-2} $\underline{M}$ NaOH

The ionic strength of each solution was approximately 0.15.

The mass-transfer characteristics of the ozone reactor were determined by measuring the volumetric mass-transfer coefficient, K_La, for oxygen using the unsteady-state reaeration method coupled with the exponential model and non-linear least-square parameter estimation [16,17]. This resulted in an oxygen K_La value of 1.05 min^{-1} at an air rate of 0.6 ℓ/min. The corresponding K_La value for ozone was estimated by assuming that the volumetric mass-transfer coefficient varied as the diffusivity to the 0.5 power.

$$(K_La)_{O3} = (K_La)_{O2}\left(\frac{D_{O3}}{D_{O2}}\right)^{0.5} \tag{4}$$

At 25°C, the Wilkie-Chang relationship [18] gave 1.89×10^{-5} cm^2/sec for D_{O3}. The tabulated diffusivity of oxygen [18] (2.5×10^{-5} cm^2/sec at 20°C) was adjusted to give 2.84×10^{-5} cm^2/sec. Therefore $(K_La)_{O3}$ was computed to be 0.86 min^{-1} or 81% of the corresponding value for oxygen which agreed well with independent measurements [10]. Gurol [10] observed a marked increase in K_La in the presence of 50 mg/ℓ of phenol in a fine-bubble reactor at low pH values. However, 50 mg/ℓ of phenol did not influence the K_La value measured in this study. Photographs were taken of the column gassed at 0.6 ℓ/min to determine [19] the surface area to volume term, a, as 0.335 cm^{-1}. This allowed the film-transfer coefficient, K_L, to be calculated as K_La/a = 2.56 cm/min = 0.043 cm/sec.

Wet Oxidation

The wet-oxidation reactor was a stirred 1.8-liter titanium vessel (Parr Instrument Company) equipped with automatic temperature control, variable-speed stirrer and tachometer. Figure 2 shows a diagram of the reactor along with the sam-

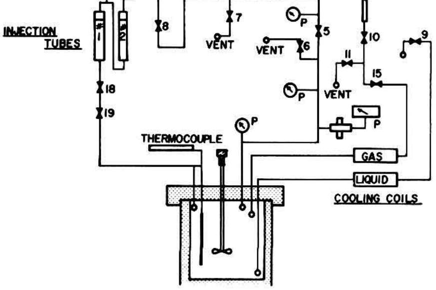

Figure 2. Schematic Diagram of experimental wet oxidation system.

pling and injection system. The reactor was charged with 900 ml of distilled water, purged with oxygen, sealed, and brought to a stable condition at the desired temperature. A 50-ml solution of reactant was loaded into injection tube 1 and a 50-ml distilled water wash was placed into injection tube 2. Injection was accomplished by pressurizing the injection system with oxygen and using this pressure to sequentially force the contents of both tubes into the reactor. The initial concentration of organic reactant was normally 5000 mg/ℓl and the initial oxygen pressure was set so that the 0.8-liter headspace contained enough oxygen to completely oxidize the reactant and still maintain at least a 0.34 MPa (50 psi) oxygen overpressure. The initial and final total pressures, therefore, depended on the reactant and the temperature. Typical values of the initial pressure were 3.9 MPa (580 psi) at 204°C, 5.2 MPa (760 psi) at 232°C, and 7.1 MPa (1050 psi) at 260°C. Liquid samples were withdrawn at times of 0, 2, 5, 15, 30, and 60 minutes, and a gas sample was taken at the conclusion of the experiment.

Analytical

Total organic carbon was measured using a Beckman 915-B Carbon Analyzer. 4-Nitrophenol was measured by liquid chromatography (LC) using a Hewlett-Packard 1084B liquid chromatograph. The LC conditions were reverse phase, water and acetonitrile for the mobile phase, using an ODS-C18 column with a UV detector at 254 nm. The other organic reactants and oxidation products were measured by gas chromatography (GC).

A Hewlett-Packard 5830 gas chromatograph was used to measure phenol, 2-chlorophenol, dichloroethane, and dimethylphthalate. The colums and conditions were:

Phenol: column Anakrom A 90/100, 5% NPGSB and 1% H_3PO_4, 1.8 m × 6.4 mm × 2 mm glass
Conditions: direct injection, injection temperature, 250°C; column temperature, 235°C; gas rate, 43 ml/min; FID

2-Chlorophenol: column: H_3PO_4 treated Porapak QS, 1.8 m × 3.2 mm glass
Conditions: direct injection; injection temperature, 225°C; column temperature, 240°C; gas rate, 5 ml/min; FID

1,2-Dichloroethane: column: same as 2-chlorophenol
Conditions: direct injection; injection temperature, 225°C; column temperature, 185°C; gas rate, 134 ml/min; FID

Dimethylphthalate: column: Tenax GC, 60 × 80 mesh 1.8 m × 6.4 mm
Conditions: direct injection; injection temperature, 250°C; column temperature, 240°C; gas rate, 16 ml/min; FID

Wet-oxidation samples were analyzed for acetaldehyde, acetone, and acetic acid using the Hewlett Packard 5830 equipment with a H_3PO_4-treated Porapak QS column. The conditions were:

direct injection; injection temperature, 250°C; column temperature, 185°C; gas rate, 23 ml/min; FID

Organic acids were measured by the procedure of Salanitro and Muirhead [*20*] in which the samples were subjected to a butyl-esterification process. Subsequently, the butyl esters were identified and measured by gas chromatography using a Hewlett Packard 5880 gas chromatograph equipped with a SP-2100, 25-mm silica capillary column. The conditions were:

splitless technique with valve interrupt of the purge for 30 seconds; temperature program, 40°C, 8°C/min for 5 minutes then 20°C/min to 250°C; gas rate, carrier gas (helium) at 5 ml/min, nitrogen auxilary makeup at 30 ml/min; FID

The chromatograms indicated the following peak retention times for the butyl esters.

Butyl Ester of	Typical Peak Retention Time, min
Formic acid	3.85
Reagent	3.9
Acetic acid	4.57
Reagent	5.64
Propionic acid	5.84 (internal standard)
Butyric acid	7.00 (reagent)
Oxalic acid	10.55
Malonic acid	11.20 (internal standard)
Maleic acid	11.92
Succinic acid	12.10
Muconic acid	14.20

RESULTS AND DISCUSSION

Evaluation of Air Stripping During Ozonation

Quantities of organic reactants removed by possible volatilization were estimated by conducting air-stripping experiments under conditions identical to those of the ozonation experiments. Decreases in organic reactant concentrations indicated removal by volatilization.

Table 1 shows the results of air-stripping experiments conducted at a gas rate of 0.6 ℓ/min on a liquid volume of 0.25 ℓ containing initial organic concentrations of 50 mg/ℓ. Relative concentration, defined as the ratio of the concentration to the initial concentration, did not decrease significantly for phenol, 2-chlorophenol (2CP), 4-nitrophenol (4NP), and dimethlphthalate (DMP). However, 1,2-dichloroethane (DCE) showed appreciable volatility as the measured relative concentration decreased by 95% during the first 30 minutes of air stripping. Because of this, no ozonation experiments were conducted using DCE. the measured relative concentrations generally agreed with relative concentrations predicted by assuming a completely mixed liquid phase with the solute in the exit gas in equilibrium with the liquid [*21*]. For this case, a mass balance for the solute gives:

$$V_L \frac{dC}{dt} = -GHC \tag{5}$$

where

TABLE 1. MEASURED AND PREDICTED RELATIVE CONCENTRATIONS DURING AIR STRIPPING

Measured Relative Concentration $= \frac{C}{C_o}$

Time (min)	Phenol	2-CP	4-NP	DMP	DCE
0	1.00	1.00	1.00	1.00	1.00
5	1.05	1.00	—	1.00	0.64
10	0.98	1.04	1.00	0.80	0.37
20	1.01	1.00	1.00	0.91	—
30	1.00	1.07	1.00	0.96	0.048
60	1.04	0.93	1.04	0.95	0.01

Predicted Relative Concentration $= \frac{C}{C_o}$

Time (min)	Phenol	2-CP	4-NP	DMP	DCE
30	0.999	0.93	0.97	0.998	0.03
60	0.998	0.87	0.93	0.997	0.0007

V_L = volume of liquid in reactor, L^3
G = volumetric gas flow rate, $L^3 t^{-1}$
H = Henry's law constant, defined by $H = C_g/C^*$, dimensionless
C^* = aqueous concentration of solute in equilibrium with gas phase, mol L^{-3}
C_g = concentration of solute in the gas phase, mol L^{-3}

Integrating gives:

$$\frac{C}{C_o} = \exp\left[-H\frac{G}{V_L}t\right] \qquad (6)$$

where C_o = aqueous concentration of solute at time zero, mol L^{-3}.

For the conditions of the stripping experiments,

$$\frac{G}{V_L} = \frac{0.6\ \ell/\text{min}}{0.25\ \ell} = 2.4\ \text{min}^{-1}$$

Equation 6 was applied with the known values of Henry's constant [22] listed in Table 2 to calculate the predicted relative concentration values listed in Table 1 for times of 30 and 60 minutes. The predicted and measured concentrations were in general agreement. The assumption that the exit gas is in equilibrium with the liquid caused the predicted relative concentrations to reflect the maximum possible volatilization. In view of this and the volatilization reflected by the measured relative concentrations, it is seen that removal of reactant by volatilization was insignificant for phenol, 4NP, and DMP. For 2CP, volatilization removed a small amount (about 10%) of the solute over 60 minutes, whereas nearly all of the DCE was volatilized.

Substance Removal Patterns During Ozonation

Figures 3 through 8 show the substance and total carbon removal patterns observed during ozonation of phenol, 2-chlorophenol, 4-nitrophenol, and dimethylphthalate at initial pH levels of 6 and 10. Even though the solutions contained a phosphate buffer, the buffer intensity was insufficient to maintain constant pH. The initial pH values of 10 and 6 decreased to about 8 and 4.5, respectively during ozonation. It is shown that the rate of reaction between ozone and the primary organic substance was limited by the rate of ozone transfer. Because of this it was not possible to determine kinetic rate constants directly from the removal patterns. For purposes of comparison, the substance and total organic carbon removal patterns were modelled by an empirical exponential equation:

$$\frac{C}{C_o} = \exp(-mt) \qquad (7)$$

where C = aqueous concentration of solute or TOC at time t, mol L^{-3}
C_o = aqueous concentration of solute or TOC at time zero, mol L^{-3}
m = removal parameter, t^{-1}

This empirical model was fitted to the substance and TOC data by nonlinear least-squares regression [*17*] and is shown by the curves on Figures 3 through 8. The solutions were prepared so that initial concentrations, C_o, of specific substances were approximately 50 mg/ℓ and the samples taken at time zero showed concentrations within 10% of this value. To allow for error in C_o, best-fit values of this parameter were estimated along with the best-fit values of m by nonlinear

TABLE 2. VALUES OF HENRY'S CONSTANT USED TO CALCULATE PREDICTED RELATIVE CONCENTRATIONS

Substance	*Henry's Constant* $\frac{\text{mol}/\ell\ \text{gas}}{\text{mol}/\ell\ \text{liquid}}$
Phenol	1.31×10^{-5}
2-Chlorophenol (2-CP)	10^{-3}
4-Nitrophenol (4-NP)	4.68×10^{-4}
1,2-Dimethylphthalate (DMP)	2×10^{-5}
1,2-Dichloroethane (DCE)	5×10^{-2}

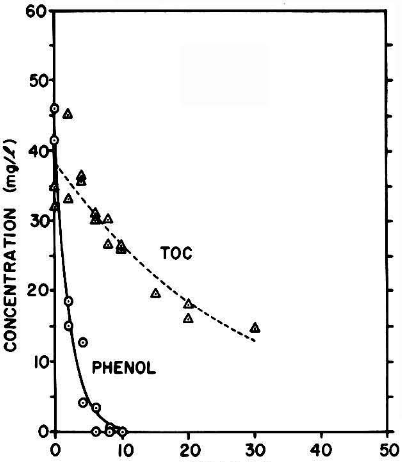

Figure 3. Phenol and TOC destruction during ozonation at pH 6.

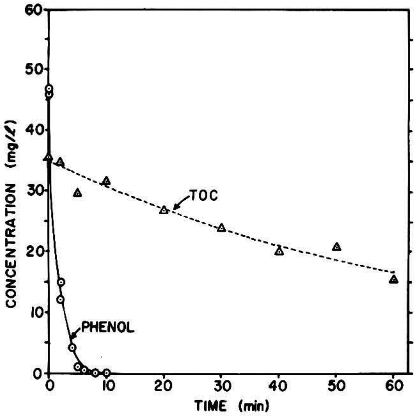

Figure 4. Phenol and TOC destruction during ozonation at pH 10.

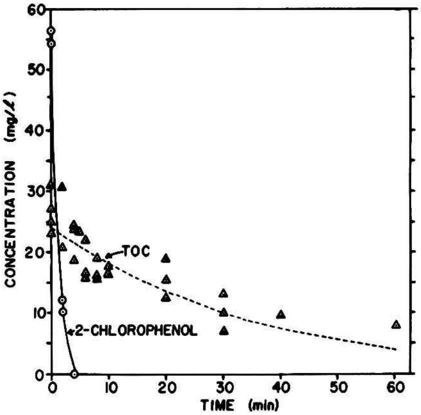

Figure 5. 2-Chlorophenol and TOC destruction during ozonation at pH 6.

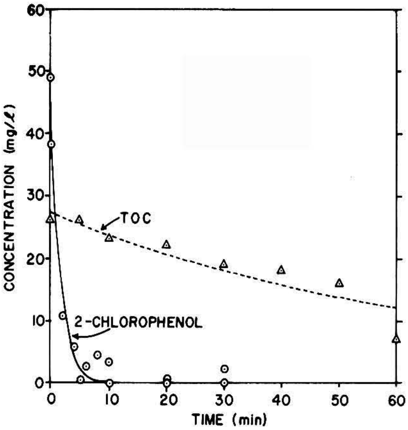

Figure 6. 2-Chlorophenol and TOC destruction during ozonation at pH 10.

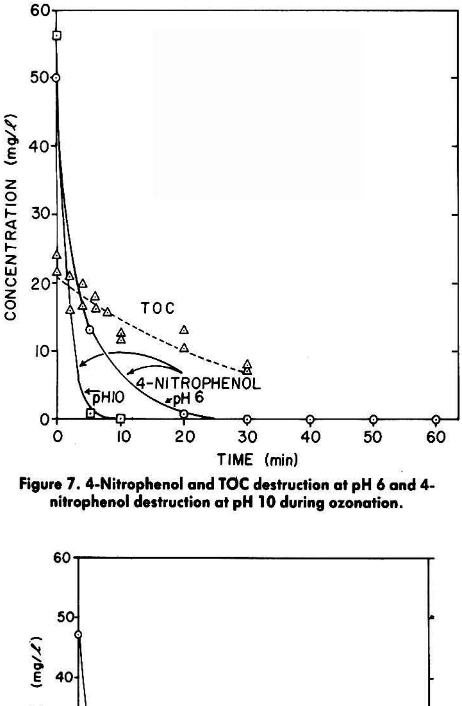

Figure 7. 4-Nitrophenol and TOC destruction at pH 6 and 4-nitrophenol destruction at pH 10 during ozonation.

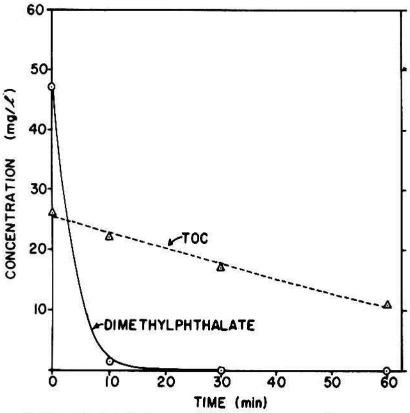

Figure 8. Dimethylphthalate and TOC destruction during ozonation at pH 6.

regression. Table 3 shows the parameter estimates which resulted from fitting the empirical exponential equation to both the specific substance and total organic carbon removal patterns. Although phenol and 4-nitrophenol showed higher values of m for specific substances under alkaline conditions, 2-chlorophenol yielded a greater specific substance removal parameter under acidic conditions. The total organic carbon (TOC) removal parameters for both phenol and 2-chlorophenol significantly decreased with increasing pH. However, at a given pH range, the TOC removal parameters of various phenolic compounds were similar. This suggests similarities between the intermediate substances formed during ozonation of the various phenolic compounds.

Caution should be used in attempting to make inferences regarding reaction kinetics from the substance rate parameters. In modelling similar data, Gurol [*10*] reported that the reactant-disappearance profile was relatively insensitive to the kinetic rate constant and depended primarily on the reactor K_L a value. The intermediate product profiles were more sensitive to the kinetic rate constants.

Ozone Consumption

During several ozonation experiments, the potassium-iodide trap through which the reactor exhaust passed was changed at intervals of 2 to 10 minutes. In this way, the average mass rate of ozone leaving the reactor could be calculated for each time interval. The mass rate of ozone fed to the reactor was known from measurements made before and after the experiment. Therefore, the ozone-utilization profile during the experiment could be determined by difference. During the first two minutes of reaction, approximately 40 to 70 percent of the ozone supplied was utilized. However, this percentage decreased rapidly after 4 minutes so that, during the period of 10 to 30 minutes, the ozone utilized was on the order of 5 percent of the amount fed. Therefore, precise calculations of ozone utilization could be made only for the first few minutes of reaction. Table 4 compares the initial rates of ozone and reactant utilization for various experiments in which ozone-utilization profiles were measured. The initial average substance-utilization rate, R_s, was calculated as,

$$R_s = V_L\left(\frac{\Delta C}{\Delta t}\right) = V_L\left(\frac{C_o}{\Delta t}\right)(1 - \exp(-mt)) \qquad (8)$$

where ΔC is evaluated as the difference between concentrations at $t = t$ and $t = 0$ as predicted by the empirical exponential model which had been fitted to the data. The initial utilization ratio, was calculated as:

$$\frac{\text{moles ozone used}}{\text{mole substance used}} = \frac{R_o\,M_s}{R_s\,M_o} \qquad (9)$$

where M_o and M_s are the molecular weights and R_o and R_s are the mass-utilization rates of ozone and substrate, respectively.

The value of the initial utilization ratio for phenolic compounds (3.9 to 5.9 moles/mole) is consistent with similar ratios observed by others. Eisenhauer [*11*] measured an ozone utilization of 3 to 4 moles of ozone per mole of phenol. Gilbert [*23*] studied the ozonolysis of mono-, di-, and tri-chlorophenols and reported an ozone consumption of 3.2 to 5 moles of ozone per mole of chlorophenol. Others [*24,9*] stated that phenolic compounds react with 3 moles of ozone per mole of compound to break the olefinic bonds. In this study, it appears that values of the utilization ratio greater than 3.0 were caused by ozone decomposition at the slightly acidic and alkaline pH conditions and by possible reaction of ozone with organic intermediates (e.g., formic acid) produced by the initial reactions of ozone and phenolic compound.

Apparent Enhancement of Mass Transfer by Simultaneous Diffusion and Reaction of Ozone

Others [*10,25*] have observed that, during ozonation of certain organic substances under semi-batch conditions, the concentration of dissolved ozone remains undetectable in the bulk liquid until the concentration of the organic substance

TABLE 3. PARAMETER ESTIMATES FOR SPECIFIC SUBSTANCE AND TOTAL ORGANIC CARBON REMOVAL PATTERNS

	Phenol		2-Chlorophenol 2-CP		4-Nitrophenol 4-NP		Dimethylphthalate DMP
Initial pH	6	10	6	10	6	10	6
Specific Substance							
Nominal C_o (mg/ℓ)	50	50	50	50	50	50	50
Estimated C_o (mg/ℓ)	44	46	55	43	50	56	47
Estimated removal parameter, m (min^{-1})	0.46	0.62	0.83	0.61	0.26	0.84	0.35
Total Organic Carbon							
Nominal C_o (mg/ℓ)	38	38	28	28	26	26	31
Estimated C_o (mg/ℓ)	38	35	25	27	21	—	26
Estimated removal parameter, m × 10^2 (min^{-1})	3.7	1.2	3.0	1.4	3.7	—	1.3

TABLE 4. INITIAL RATES OF OZONE AND REACTANT UTILIZATION

		Initial Utilization Rates (0 to 2 min.)			
Substance	Initial pH	Ozone, R_o (mg/min)	Substance, R_s (mg/min)	Initial Utilization Ratio (mol ozone/mol substance)	Apparent Enhancement Factor
Phenol	6	6.6	3.3	3.9	3.3
2-Chlorophenol	6	10.1	5.6	4.8	5.0
2-Chlorophenol	10	8.3	3.8	5.9	4.1
4-Nitrophenol	6	5.4	2.5	5.9	2.7
4-Nitrophenol	6	5.3	2.5	5.8	2.6
1,2-Dimethylphthalate	10	3.7	—	—	1.9

decreases close to zero. Although dissolved ozone was not measured in this study, it is suspected that the dissolved ozone concentration remained close to zero until the initial organic reactants had disappeared. Under these conditions, it is possible for the reaction in the diffusive film to increase the concentration gradient of ozone and thereby enhance mass transfer. For the case of a second-order reaction between a diffusing dissolved gas, A, and a dissolved substance, B, such as that between ozone and dissolved organics,

$$A_{(O_3)} + zB_{(org)} \xrightarrow{k_o'} \text{products} \tag{10}$$

Dankwerts [26] has shown that the amount of diffusing gas which reacts in the film will be negligible in comparison to that which reacts in the bulk liquid if:

$$\frac{D_A\, k_o'\, C_B}{K_L^2} \ll 1 \ll \frac{k_o'\, C_B}{K_L\, a} \tag{11}$$

where

D_A = diffusivity of the diffusing gas, $L^2\, t^{-1}$

k_o' = second-order rate constant, mol $L^{-3}\, t^{-1}$ ($k_o' C_B O_3$ = moles A/time)

C_B = concentration of dissolved substance in the bulk liquid, mol L^{-3}

K_L = film mass-transfer coefficient for the diffusing gas, L t^{-1}

$K_L\, a$ = volumetric mass-transfer coefficient for the diffusing gas, t^{-1}

If this condition is not met, a significant fraction of the diffusing gas will react in the film and this simultaneous diffusion and reaction will cause the rate of mass transfer to be enhanced by a factor E, the enhancement factor, given approximately by [26]:

$$E = \frac{\left[M \frac{E_i - E}{E_i - 1}\right]^{0.5}}{\tanh\left[M \frac{E_i - E}{E_i - 1}\right]^{0.5}} \tag{12}$$

where

$$M = \frac{D_A k_o' C_B}{K_L^2}$$

$$E_i = \left[1 + \frac{D_B C_B}{z D_A C_A'}\right]$$

D_B = diffusivity of the dissolved reactant, $L^2\, t^{-1}$

C_A' = equilibrium concentration of the diffusing gas in the liquid, mol L^{-3}

The maximal ozone-transfer rate, W, based on the $K_L\, a$ value measured for ozone in the absence of reaction is determined by:

$$W = (K_L\, a)(V_L)(C_{O_3}') \tag{13}$$

The ozone content of the gas stream was typically 25 mg/ℓ. Based on this value, and a solubility coefficient of 0.37 mg/ℓ in liquid per mg/ℓ in gas[10] at 25°C, C_{O_3}' is calculated as 9.25 mg/

ℓ, and the maximal transfer rate in the absence of reaction is:

$$(0.86\ 1/\text{min})(0.25\ell)(9.25\ \text{mg}/\ell) = 2.0\ \text{mg/min}$$

This is clearly less than the measured ozone-utilization rates listed in Table 4, indicating an apparent enhancement of the transfer rate in the presence of reaction. The apparent enhancement factors listed in Table 4 were calculated by dividing the measured initial ozone-utilization rate by the maximal transfer rate in the absence of reaction, 2.0 mg/min.

It has been reported [*10*] that the reaction-rate constants for ozonation of phenol and phenolate are 1.1×10^3 and 4×10^7 $\ell/(\text{mol}\cdot\text{sec})$, respectively. Because the pK of phenol (corrected for an ionic strength of 0.15) is 9.6, the reaction rate would be expected to increase markedly as the pH increased above 6.

At pH values of 6.6, 7.6, 8.6, and 9.6; 0.1%, 1%, 10%, and 50%, respectively, of the total phenolic concentration would be present as phenolate ion. Assuming that ozone is used only by direct reaction with phenol and phenolate, Equation 12 can be evaluated for the conditions prevailing during the first two minutes of the ozonation experiments, where the total phenolic concentration was roughly 40 mg/L. The results of this calculation are shown in Table 5 and, at pH 6, indicate an enhancement factor of only 1.06, considerably lower than the value of 3.3 measured for phenol at pH 6. Based on this, it appears that ozone decomposition or reaction with intermediate products may cause E to be greater than predicted based upon reaction with only phenol and phenolate.

Wet Oxidation Results

Figures 9 and 10 show profiles of phenol and 2-chlorophenol, respectively, during wet oxidation at temperatures of 204°C, 232°C, and 260°C. The corresponding profiles for total organic carbon are given by Figures 11 and 12. The data indicate a relatively rapid removal of phenol and a substantially slower removal of 2-chlorophenol. The total organic carbon data also indicate slower removal for 2-chlorophenol. Initial pH and copper catalyst also influence the reaction [5].

For purposes of comparison, substance removal during wet oxidation was modelled by Equation 7. Table 6 shows the resulting best-fit estimates for the removal parameters for the five compounds investigated. The removal parameters vary considerably between substances and increase markedly with increasing temperatures. Interpretation of these data in light of the second-order kinetics given by Equation 3 requires consideration of:

1. the change in oxygen pressure during the experiment
2. possible volatilization of reactant into the headspace
3. dissolved oxygen concentration as influenced by the volumetric mass-transfer coefficient

TABLE 5. CALCULATED VALUES OF THE ENHANCEMENT FACTOR ASSUMING THAT OZONE IS USED ONLY BY REACTION WITH PHENOL AND PHENOLATE.

pH	$\frac{D_A k_o C_B}{K_L^2}$	E
6.6	0.18	1.06
7.6	1.75	1.45
8.6	17.5	2.9
9.6	87.4	4.05
10.6	175	4.35

$K_L = 0.043$ cm/sec
$D_{phenol} = 10^{-5}$ cm²/sec
$D_{ozone} = 1.9 \times 10^{-5}$ cm²/sec
$z = 1/3$
$A^* = 9.25$ mg/ℓ
$E_i = 4.81$

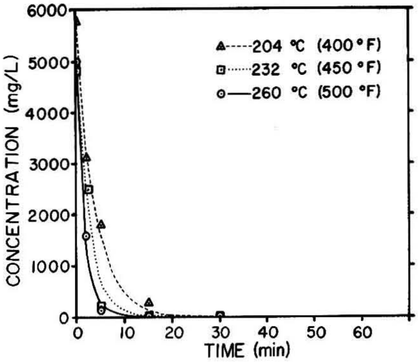

Figure 9. Influence of temperature on phenol destruction, pheno concentration versus time.

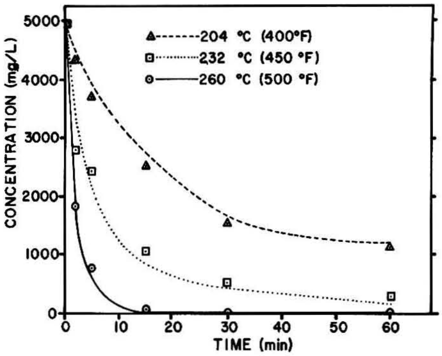

Figure 10. Influence of temperature on the destruction of 2-chlorophenol, concentration versus time.

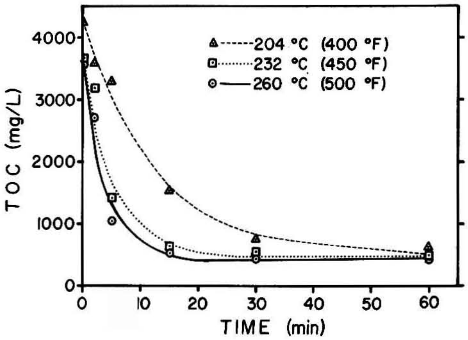

Figure 11. Influence of temperature on phenol destruction, TOC versus time.

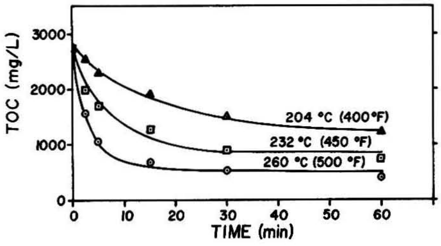

Figure 12. Influence of temperature on 2-chlorophenol destruction, TOC versus time.

Table 6. Summary of Removal Parameters, m min^{-1}, During Wet Oxidation

	Temperature		
	204°C	232°C	260°C
Phenol	0.25	0.42	0.59
2-Chlorophenol	0.035	0.12	0.45
4-Nitrophenol	0.04	0.27	0.94
1,2-Dimethylphthalate	0.008	0.036	0.100
1,2-Dichloroethane	0.45	0.85	1.02

Initial oxygen pressures were on the order of 2 to 2.5 MPa (288 to 360 psi) and decreased to 1 to 1.5 MPa (144 to 216 psi) during the course of reaction as liquid samples were withdrawn and oxygen was utilized. This variation in pressure apparently had little effect on the reaction rate, because removal parameters estimated using only the first three data points were only slightly greater than those given in Table 6.

The influence of volatilization can be significant if a large fraction of the reactant resides in the reactor headspace. This can be analyzed by a reactant material balance based on equilibrium between the liquid and vapor phases:

$$-rV_L = V_L \frac{dC}{dt} + V_G \frac{dC_g}{dt} \tag{14}$$

where V_G = volume of gas in the reactor headspace, L^3

The measured reactant profile reflects concentration of liquid phase, C, as a function of time and was described by $dC/dt = -mC$.

Assuming that the reactant in the vapor phase is in equilibrium with the liquid gives:

$$\frac{dC_g}{dt} = \frac{d(HC)}{dt} = H\frac{dC}{dt} = -HmC \tag{15}$$

so that Equation 14 can be written as:

$$r = m\left[1 + \left[\frac{V_G}{V_L}\right] H\right] C \tag{16}$$

Comparison with the second-order rate expression (Equation 3) shows that:

$$k_w (O_2) = m\left[1 + \left[\frac{V_G}{V_L}\right] H\right] \tag{17}$$

Provided that reasonable values of Henry's constant, H, can be estimated at elevated temperatures, Equation 17 allows the product k_wO_2 to be determined from the measured value of r. It has been shown [27] that H can be related to the vapor pressure and aqueous solubility of a pure substance. Assuming that the solubility, C^*, is constant with increasing temperature facilitates rough estimates of H at elevated temperatures by:

$$\frac{H_1}{H_2} = \frac{P_{v1}}{P_{v2}} \frac{T_2}{T_1} \frac{C_2^*}{C_1^*} \tag{18}$$

where P_{v1} and P_{v2} are vapor pressures of the pure substance at temperatures T_1 and T_2 respectively. Using this approach gives rough H values at 0.057 mol/mol and 5.8 mol/mol for phenol and dichloroethane respectively at 204°C. Evaluation of Equation 17 for these substances at 204°C shows that volatilization is insignificant for phenol as $k_wO_2 = 1.04m$, but extremely significant for dichloroethane as $k_wO_2 = 5.67m$.

Pruden and Le [*13*] estimated $k_w = 3146\ \ell/(\text{hr}\cdot\text{mol})$ for phenol at 200°C. The initial dissolved oxygen in the wet-oxidation reactor can be estimated based on this rate constant as:

$$O_2 = \frac{1.04m}{k_w} = \frac{1.04(0.25\ 1/\text{min})(60\ \text{min/hr})}{3146\ \ell/(\text{hr}\cdot\text{mol})} = 4.96 \times 10^{-3}\ \frac{\text{mol}}{\ell}$$

which is 13% of the saturation value [*28*]. This indicates that, under these experimental conditions, reaction in the diffusive film would not be significant.

Products of Reaction

Figures 13 and 14 show organic-acid profiles during ozonation of 50 mg/ℓ phenol and 1000 mg/ℓ 2-chlorophenol (2-CP) respectively. In both cases, formic and oxalic acids were observed to be important intermediate and end products. Total Organic Carbon (TOC) measurements indicated that, for phenol at 50 mg/ℓ, the acids measured accounted for 60 to 80 percent of the organic carbon present. However, for 2-CP at 1000 mg/ℓ, the acids measured only accounted for 26 to 42 percent of the organic carbon measured. The remaining portion of the organic carbon presumably consisted of substances other than organic acids. Aldehydes were not measured and could have accounted for much of the remaining organic carbon. In addition to the four acids shown in Figures 13 and 14, (formic, oxalic, muconic, and maleic) standards were run for acetic and succinic acids, but these acids were not detected in the ozonated samples. Various additional peaks were detected on the chromatograms of the esterified samples, but were not

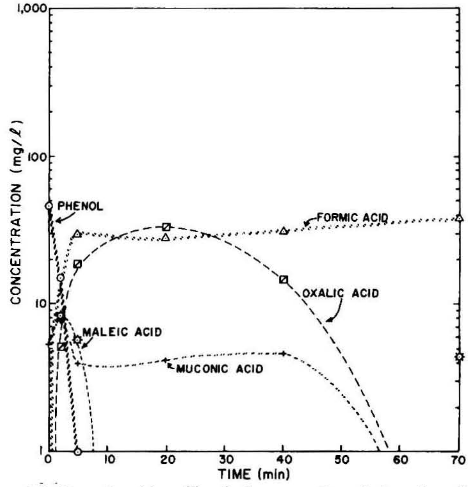

Figure 13. Organic acid profiles during ozonation of phenol at pH 10.

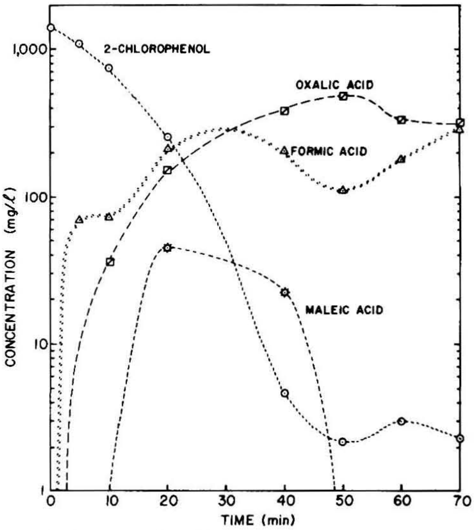

Figure 14. Organic acid profiles during ozonation of 2-chlorophenol at pH 10.

identified. Two of these at retention times of 4.63 and 10.61 minutes were consistently present. These were not identified, but, based on relative retention times, the 4.63 minute peak could have been glycolic, glyoxylic, or pyruvic acids. Although catechol and hydroquinone were expected from phenol, they were not found, presumably because they could have been present very early in the reaction and been missed or they could have been present at concentrations below the detection limit.

Comparison of Figure 13 to similar data obtained for phenol by Yamamoto *et al.* [3] indicates a substantially faster rate of phenol utilization and acid production in this study, presumably because of a higher ozone dosage rate. Similar concentrations of formic and oxalic acids were observed in each study. The decrease in oxalic acid concentration in the presence of formic acid indicated in Figure 13 at times greater than 40 minutes was not observed by Yamamoto *et al.* This might be attributable to differences in pH values, dosage rates, and temperatures between the two studies.

Figures 15 and 16 show profiles of organic-carbon transformation during wet oxidation of phenol and 2-chlorophenol at 232°C. The initial concentrations in each case was 5000 mg/ℓ, which is substantially higher than the initial concentration in the ozonation experiments. Also, the wet-oxidation experiments were essentially unbuffered; the initial pH was 4.5 and this decreased to 2.5 during the reaction period. Acetaldehyde and acetone were measured in addition to the organic acids. For phenol, essentially all (83% to 105%) of the TOC was accounted for by the individual species measured at 15 to 60 minutes. However, for 2-chlorophenol, only 72 to 86% of the TOC was accounted for by the individual species.

Comparison of the wet-oxidation and ozonation organic-acid profiles indicates that, in both cases, acetic acid was not evident during ozonation, although it was a major end product of wet oxidation. Conversely, oxalic acid was a relatively minor product during wet oxidation, but was an important product of ozonation.

SUMMARY AND CONCLUSIONS

Semi-batch ozonation experiments showed that:

1. All four specific pollutants studied could be removed completely (in 5 to 10 minutes) through ozonation. However, the removal rates were limited by the rate of ozone mass transfer.

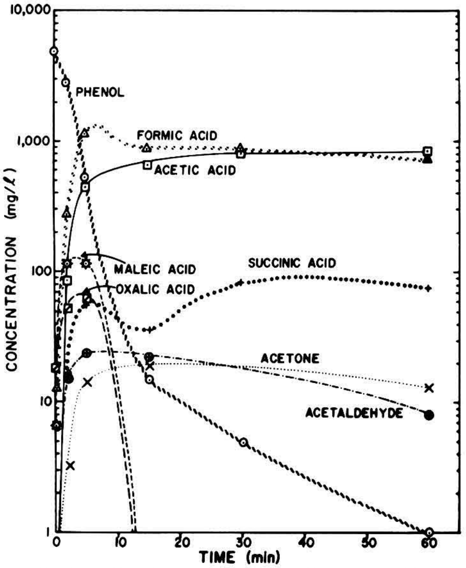

Figure 15. Organic carbon transformations during wet oxidation of phenol at 232°C.

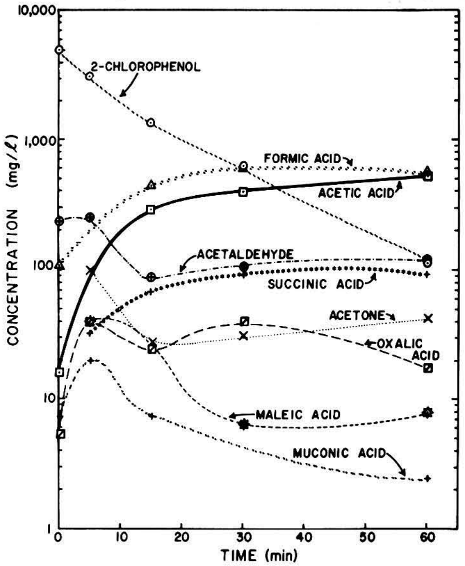

Figure 16. Organic carbon transformations during wet oxidation of 2-chlorophenol at 232°C.

2. During the initial stages of the ozonation experiments, reaction in the diffusive film enhanced the mass-transfer rate.
3. A significant amount of total organic carbon remained in solution after the specific pollutants had been removed and this carbon was slowly oxidized. Formic, oxalic, muconic, and maleic acids accounted for roughly one-quarter to three-quarters of the organic carbon remaining.
4. Initial ozone utilization ratios showed that 3.9 to 5.9 moles of ozone per mole of specific pollutant were consumed.
5. Increasing the initial pH from 6 to 10: a) increased the specific pollutant removal rate for phenol and 4-nitrophenol, but decreased the rate for 2-chlorophenol; b) decreased the total organic carbon removal rates for phenol and 2-chlorophenol.

Batch wet-oxidation experiments showed that:

1. All five specific pollutants studied could be oxidized under the conditions of temperature and oxygen pressure studied. The removal rates depended on the substance and on the temperature.
2. Reaction in the diffusive film probably did not enhance the mass transfer of oxygen in the stirred-unsparged pressure reactor.
3. A significant amount of total organic carbon remained in solution after the specific pollutants had been removed and this carbon was slowly oxidized. More than three-fourths of this carbon was accounted for by low-molecular weight acids, acetaldehyde, and acetone.

Although acetic acid was a major end product of wet oxidation, it was not evident during ozonation. Conversely, oxalic acid was a relatively minor product during wet oxidation, but was very significant in ozonation.

ACKNOWLEDGEMENT

This project was partially supported by the U.S.E.P.A., Grant Number R805565-010, the Center for Waste Management Programs, and the Department of Civil Engineering at Michigan Technological University. We wish to express our gratitude to Richard Lamparter, Co-director of the Center for Waste Management Programs, and to Timothy Geiger for conducting the wet-oxidation experiments.

NOMENCLATURE

Dimensions and Units

°C = degrees Celsius
cm = centimeter
ℓ = liters
L = length
$\underline{M}$ = molarity
mg = milligram

ml = milliliter
mm = millimeter
mol = gram mol
MPa = mega pascal
nm = nanometer
psi = pounds per square inch

Symbols

a = interfacial area per unit volume, L^{-1}
C = aqueous concentration of organic reactant or TOC at time t, mol L^{-3}
C_o = aqueous concentration of reactant at time zero, mol L^{-3}
C^* = aqueous concentration of substance in equilibrium with gas phase, mol L^{-3}
C_g = concentration of substance in the gas phase, moles per unit volume of gas, mol L^{-3}
D = diffusivity of substance in water, $L^2\ t^{-1}$
E = mass-transfer enhancement factor, ratio of K_La in presence of reaction to K_La with no reaction, dimensionless
E_i = $\left[1 + \frac{D_B C_B}{z D_A C_A^*}\right]$, dimensionless
F = ozone dosage rate, moles of ozone fed per unit time per mole of phenol initially present, mol O_3 (mol phenol)$^{-1}$ t^{-1}
FID = flame-ionization detector
G = volumetric gas flow rate, $L^3\ t^{-1}$
H = Henry's Law constant, C_g/C^*, dimensionless
K_c = combined rate constant, mol phenol (mol ozone)$^{-1}$
K_L = overall mass-transfer coefficient based on the liquid film, L t^{-1}
K_La = overall volumetric mass-transfer coefficient based on the liquid film, t^{-1}
k_o = second-order reaction-rate constant for ozonation, gives r in terms of organic reactant, L^3 $mol^{-1}\ t^{-1}$
k_o' = second-order reaction-rate constant for ozonation, gives r in terms of ozone, mol $L^{-3}\ t^{-1}$
k_w = second-order reaction-rate constant for wet oxidation, $L^3\ mol^{-1}\ t^{-1}$
M = $(D_A)(k_o')(C_B)/K_L^2$, dimensionless
m = removal parameter, t^{-1}
M_s = molecular weight of substance, mass mol^{-1}
M_o = molecular weight of ozone, mass mol^{-1}
O_2 = aqueous concentration of oxygen, mol L^{-3}
O_3 = aqueous concentration of ozone, mol L^{-3}
P_v = vapor pressure
R_s = rate of substance utilization, mass t^{-1}
R_o = rate of ozone utilization, mass t^{-1}
r = rate of reaction of organic per unit volume, mol $L^{-3}\ t^{-1}$
t = time
T = temperature
V_L = reactor liquid volume, L^3
V_G = reactor headspace volume, L^3
W = maximal ozone transfer rate, mass t^{-1}

Subscripts

1,2 denote temperatures 1 and 2, respectively, used with P_v, T, H, and C^*

A,B deonote substance A and B, respectively, used with D,C, and C^*

O2,O3 denote oxygen and ozone, respectively, used with K_La, C^*, and D

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Centralized Treatment of Industrial Wastes

An intercompany pooling operation can significantly reduce the cost of treatment on site in individual processing operations.

Edward R. Saltzberg, JRB Associates, McLean, Va. 22101

Typically, an industrial firm will meet a government wastewater discharge standard by installing an end-of-pipe treatment system. More often than not this approach is expensive; the equipment is hard to operate efficiently and it generates a sludge which then may subject the firm to hazardous-waste regulations. None of these results are particularly appealing. Fortunately, there is a low-cost and effective alternative to on-site treatment which can be used by firms in many areas of the country. This alternative is centralized waste treatment.

Under the CWT approach, firms would send their wastes to a common processing plant. Figure 1 shows how the system works. In the right situations and with the proper kind of inexpensive retrofitting measures, CWT can drastically reduce the cost of treating industrial wastewater because of economies of scale. As well as saving money, CWT has several environmental advantages. First, these facilities are operated by professional waste handlers who should be able to treat and manage the waste more effectively than the generating firms. Second, the CWT can dramatically increase the potential for recovery of chemicals, which not only reduces the firm's wastewater costs but also the burdens of sludge handling and disposal. Additionally, under some CWT concepts, firms can share other services to further reduce their operations.

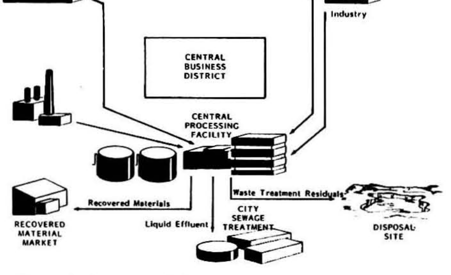

Figure 1. Overview of the central waste treatment system.

EPA, consultants, and local communities have been working on this concept for the last three years. During that time, they have been studying the feasibility of several CWT alternatives already in use in foreign countries for treating electroplating wastewater. Under one option, firms ship their wastes by truck to a centralized facility for processing. This concept is being pursued in Providence, Rhode Island, and Cleveland, Ohio. It is modelled after a system used in Germany.

An alternative technique is for the firms to move to a central location, either in an industrial park or a specially designed building. This concept is being actively studied in Brooklyn, New York, again for electroplating firms, and is currently used in Japan. In addition to waste treatment, Brooklyn's "Plating City" can also provide cogeneration of power, common laboratory facilities and, probably a bulk purchasing cooperative.

APPLICATION OF CWT TO INDUSTRY

GENERAL CONSIDERATIONS

The central waste-treatment concept is not limited to any particular industry. However, certain industrial, regional, and regulatory characteristics favor CWT more than others. Six important characteristics are:

- Number of participants
- Location of participants
- Transportation and access
- Amount of waste from each plant
- Size of participating firms
- Enforceable regulations

The first characteristic is important because of economies of scale. The more firms that participate in a central facility, the lower is the unit cost of treatment.

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Hauling cost is a major part of the CWT charge in the German central treatment concept. Accordingly, the second characteristic, the location of CWT users, controls, to a large extent, the cost effectiveness and overall feasibility of a central treatment facility in a locality. Results from a recent study by the CENTEC Corporation and JRB Associates for EPA show how large and variable an impact transportation can have on CWT costs. Estimates of hauling costs in five cities studied in that project range from 17.2 to 43.3 percent of total CWT costs for electroplating shops.

Good roads and easy access to the users by tank truck is also an important factor which favors CWT (in the German model). Firms with poor waste pickup sites in cities with narrow, winding roads are not good candidates for CWT. Also firms in the snow belt of the United States would require large storage facilities to protect themselves against pickup delays and cancellations during bad weather. In some instances, this added cost may make on-site treatment less costly than CWT. As a result, the plating-city concept may have an advantage over the other CWT concept in these regions.

The third characteristic favoring CWT is small volumes of concentrated wastes. Generally, CWT only helps companies with small flows because firms with large waste flows will be able to benefit from economies of scale by installing their own waste-treatment systems. In some cases, the cost savings from CWT for large companies are not enough to offset transportation costs to the central facility. Since transportation costs in a CWT system are a function of the distance to the facility, there exists a maximum volume above which CWT is not economical. Therefore, when examining the applicability of CWT, it is important to consider not only waste volumes currently being generated but also the potential for volume reduction. In some industries, firms use more process water than necessary. Recovery/recycle technologies and housekeeping practices can reduce or concentrate waste flow to a fraction of their current size making CWT more economical. Through waste reduction, many large firms can become candidates for CWT.

Pollution control equipment is expensive and firms treating on-site must have the ability to raise a great deal of capital in order to meet wastewater regulations. Generally, small firms lack this ability, which is another reason why CWT is most applicable to them. With CWT, firms do not have to buy expensive end-of-pipe treatment equipment. For the most part, they can retrofit their plants for CWT using waste-reduction techniques and installing small storage facilities. Usually these measures are not a large burden for the firm because they are cheap enough to be paid for out of cash receipts. Accordingly, firm size, measured by employment or gross sales, is an indicator of the feasibility of CWT.

All of the characteristics discussed above are important to consider in assessing the application of CWT. However, regardless of how positive they are, CWT is not likely to be implemented unless wastewater regulations are in effect and enforced. Likewise, enforcement is a driving force for on-site pollution control. That is not to say that firms do not cut back on waste discharges for other reasons. For example, many firms have turned to waste reductions to save money on water and chemicals. Also, some firms treat their wastes as a result of public pressure or because they feel the social responsibility to do so.

However, most firms reduce wastewater in order to meet government regulations. Accordingly, the fifth characteristic is among the most important in assessing the feasibility of CWT in a municipality.

Based on these characteristics, the electroplating industry is a primary candidate for centralized treatment. A recent study that JRB Associates completed for EPA showed that others include: paint manufacturing, leather tanning, porcelain enameling, and textiles.

STUDIES OF CWT IN THE UNITED STATES

There are very few central treatment facilities in the United States which process wastewater. Most existing waste management firms accept solid waste and concentrated liquid wastes, such as sludge from manufacturing and waste-water-treatment systems, spent process solutions and residues from chemical holding tanks. Centralized treatment of wastewater as an alternative to meet pretreatment and direct discharge regulations is still in the study stage in the United States.

All of the work on CWT has focused on electroplaters and has been funded by EPA or the Department of Commerce. These studies fall into two categories.

1) Studies of the application of the German approach which is shipping rinses, sludges, and spent solutions to a central facility

- EPA 5-city study
- Follow-up study of Cleveland
- Providence area-wide study

2) Studies of the application of the Japanese approach of centrally locating the participating firms

- Brooklyn's "Plating City"
- Huntington Industrial Park Group Treatment, Providence, Rhode Island

Treatment Options

The results of these studies are very dramatic. They all conclude that the CWT option is a cheaper way to treat electroplating wastewater than is the standard method of end-of-pipe treatment. In each of the studies, the CWT facility could be used to process all or part of the firm's waste. Small firms generally would be fully serviced by the facility, while larger firms may find it more economical to treat some of their wastes themselves. The various options available to participating firms are depicted in Figure 2.

In Option 1, the shop does not discharge contaminated process waters to the municipal sewer system. The concentrated rinse waters and batch dumps for all waste streams are hauled to a central waste facility for treatment. The sludge from waste treatment is dewatered at the CWT facility to approximately 20 percent solids and is hauled to a landfill.

Shops that select Option 2 would treat the cyanide and acid/alkali waste streams in-house (CN destruction, pH adjustment/precipitation) and send the dilute waste-treatment sludge (approximately 4 percent solids) and raw chromium waste stream to a CWT facility. The facility would properly treat the chromium waste stream, dewater the sludge, and haul the solids to a landfill.

Option 3 is similar to Option 2 except that the chromium and acid/alkali waste streams are treated in-house and the cyanide waste stream and sludge are hauled to a CWT facility.

In Option 4, the shop chooses to treat all waste streams in-house and to send only the dilute sludge to CWT for dewatering.

Under Option 5, the shop is not utilizing CWT. Instead, all waste treatment and sludge dewatering is done in-house.

Option 0, utilized in the Cleveland regional analysis only, represents the installation by shop of ion exchange for treatment of mixed wastewater, with the alkali and acidic regenerant backwash send to the CWT facility.

Cost Savings through CWT

Study results from the EPA 5-city project illustrate the magnitude of the possible savings from CWT. In that project, CENTEC, with help from JRB, developed a computer

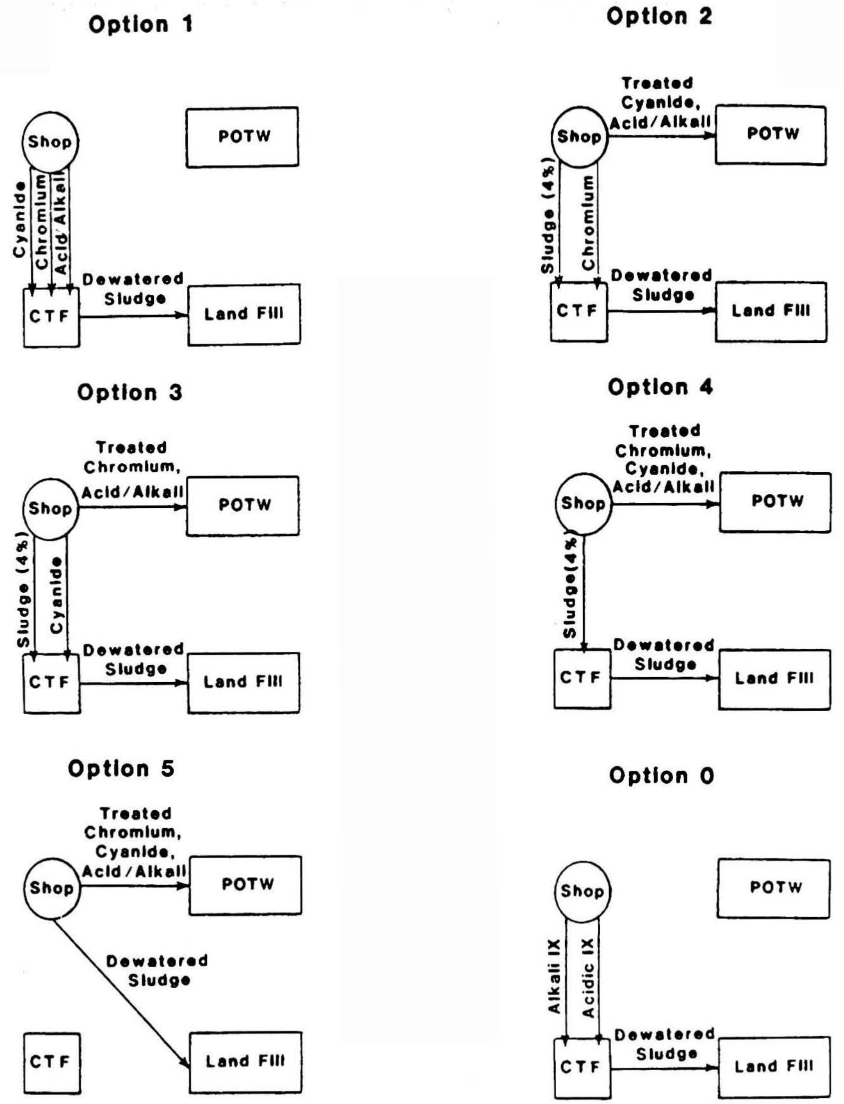


Figure 2. Waste treatment alternatives.

model which uses municipal information and data from the participating firms to 1) determine and price the least cost option for each participant, 2) locate, size, and price the CWT facility, 3) aggregate costs for each city. Estimates for the five cities are:

Region	Participation[1]	Annual Total[2] Regional Costs w/o CTF	Annual Total[3] Regional Costs w/CTF	% Savings
Cleveland	102/103	$4.2 million	$2.5 million	40
Milwaukee	23/23	1.9 million	1.4 million	26
Philadelphia	22/22	3.2 million	2.8 million	13
Atlanta	19/19	.8 million	.5 million	38
Seattle	11/11	.7 million	.5 million	29

The same computer model was used to examine the feasibility of siting a CWT facility in an industrial park in Providence. The study estimated that the cost of the treatment for the ten jewelry manufacturers in Huntington Park could be reduced by 30 percent through centralized treat-

[1] Participation is defined as reliance on CWT by a discharger or at least partial treatment of wastes. Treatment options allowed were: all waste to CWT chrome waste and all sludges to CWT, nothing to CWT.

[2] Total annual regional costs consist of annualized plant investment (assuming a required rate of return of 20 percent and 10-year equipment life), and plant operating and chemical costs.

[3] Total annual regional costs consist of annualized plant investment (assuming a required rate of return of 20 percent and 10-year equipment life), plant operating and chemical costs, transport costs, and CWT fees.

ment.

As dramatic as these estimates are, they underestimate the cost savings which can be gained through centralized waste treatment. One reason for this is that sludge disposal costs are not included in these estimates. Also, they do not consider recovery of metals which, while not practical for most electroplating firms generating small amounts of waste, can be economical in the large volumes handled by a CWT facility. In fact, results of the Providence Area-wide Study point toward a plant retrofitting technique which can be used to facilitate metals recovery at a central treatment plant. This technique is examined in the following section.

DESIGNING THE CWT FACILITY FOR METALS RECOVERY

The following low-cost method of compliance with the Pretreatment Regulations was a major product of the Providence Study. This method is applicable to most kinds of electroplating operations. A typical process diagram is shown in Figure 3. A rinse station follows each process element. The basic principle behind the Providence method is that, by controlling the plating and rinsing processes themselves more closely, the waste-treatment problem can be substantially reduced. Specifically, a change in the method of rinsing and segregation of rinses as well as direct recovery of dragout material can reduce the volume of solution requiring treatment to less than 2 percent of the normal rinse-water flow.

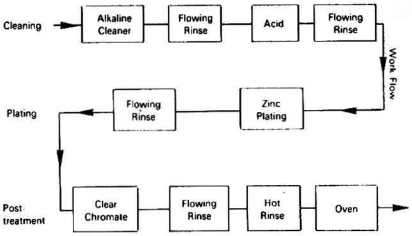
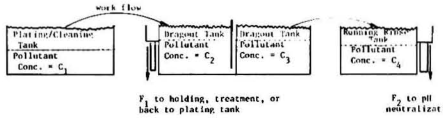


Figure 3. A typical electroplating process.

The Rinsing Method

The key to the method is a basic rinsing system designed to remove the majority of contaminating dragout in a small volume before a flowing rinse can run at a normal rate to ensure good product quality. A very simplified diagram of the rinsing system is illustrated below:



The system is very simple. By controlling the concentrations in the dragout tanks and the flow rate in the single running rinse, the level of contamination in the rinsewater can be kept so low that it does not require treatment (other than neutralization). The dragout tank concentrations are maintained in several ways:

- **By returning the solution back to the process, which is effective for hot processes because of evaporation losses.**
- **By bleeding or batch dumping the dragout to a holding tank for treatment or recovery.**
- **By a combination of the above.**

Most pollution control plans for plating shops call for treatment of large volumes of fairly dilute wastewater. This method generates small volumes of very concentrated solutions. As a result it significantly reduces the cost of treatment on site. A subcontractor to the author's firm (JRB) prepared for us a case study of a system they recently installed in Providence. They were able to reduce the plant's capital costs by 50 percent using this method. Operating costs are not yet available.

Implication for CWT

In past studies of CWT, metals recovery has not been shown to be practical. The reason for this is that the facilities were designed to handle dilute rinse waters and sludges containing several kinds of metals. Recovery of individual metals from these wastes in analogous to mining low-grade ore. It's too expensive.

On the other hand, using the method from the Providence Study, firms could store separately the dragout from each process which could not be returned to the plating bath. These solutions are rich in metals which could be sent to a central treatment plant for recovery. This is like mining high-grade ore. If enough concentrated solution is handled by the CWT, it may pay to recover the metals.

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He holds a Bachelor's Degree in Chemical Engineering from Rensselaer Polytechnic Institute, a Master's Degree in Hydrology from Boston University, and a Ph.D. in Resource Economics from the University of Virginia. He specializes in environmental management and water resource planning. He has worked in the petroleum industry as a development engineer and has been a consultant for the electroplating industry for several years.

AIChE ENVIRONMENTAL DIVISION NEWSLETTER

Environmental Division (1970)

It shall (a) further the application of chemical engineering in the environmental field; (b) provide, in cooperation with the national Program Commitee, suitable programs on environmental topics of current interest; (c) provide a communication medium for chemical engineers and other individuals to exchange nonconfidential information concerning all facets of environmental activity; (d) promote publication of papers of interest to chemical engineers in environmental activities; (e) coordinate the Institute's activities with other societies active in the environmental field; (f) act as a source of information for chemical engineers who are not actively engaged in the environmental field to bring to their attention the importance of concern for the environment, the need for its consideration in the design and operation of process plants, and opportunities in research and design of equipment and processes to solve environmental problems; (g) encourage chemical engineering educators to place suitable emphasis on protecting our environment and encourage excellence in courses in environmental engineering.

ENVIRONMENTAL DIVISION

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AIChE CONTINUING EDUCATION COURSES ON THE ENVIRONMENT DURING 1982

Advanced Waste Water Treatment

Cleveland, August 28-29
Los Angeles, November 13-14

Air Pollution Control

Cleveland, August 27-29
Los Angeles, November 12-14

Hazard Control in the Chemical and Allied Industries

Cleveland, August 30-31
Los Angeles, November 15-16

Hazardous Waste Management

Los Angeles, November 17-18

Industrial Water Conditioning

Cleveland, August 30-31
Los Angeles, November 15-16

Integrated Hazardous Waste Management

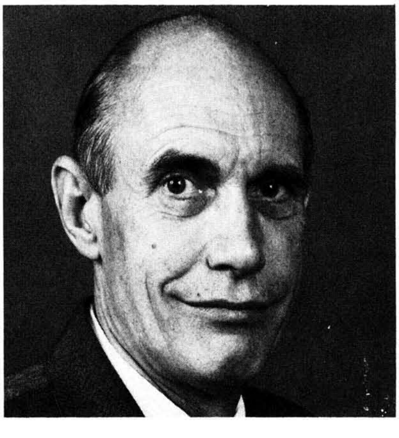
Los Angeles, November 17-18

Land Treatment of Hazardous and Non-Hazardous Industrial Wastes

Los Angeles, November 17-18

Water Quality Engineering for Industry

Cleveland, August 26-27
Los Angeles, November 11-12



ENVIRONMENTAL DIVISION AWARD-1982

The AIChE Environmental Division Award in Chemical Engineering recognizes and encourages individual outstanding chemical engineering contributions toward the preservation and/or improvement of man's natural environment. The accomplishment may be in air, water, or land pollution control or remedy. The award consists of a certificate and a prize of $1,000, donated by Battelle Memorial Institute since the award's inception in 1972.

On Monday, August 30 at the Annual Award Dinner of the Environmental Division, **Burton B. Crocker** will receive this great honor. Burt is a Distinguished Engineering Fellow in the Engineering Technology Section of Monsanto Company's Corporate Engineering Department, St. Louis, Missouri. He has had 28 years' experience in the air pollution control of chemical processes and 37 years' experience in process design and development. In Engineering Technology, he is responsible for consulting in and developing technology in air pollution control, environmental control of hazardous materials, gas-solids contacting and separation, and solids processing.

Air Section Activities

The Environmental Division program for the AIChE Diamond Jubilee meeting in Washington, D.C., from October 31 to November 4, 1983, will include four sessions sponsored by the Air Section. These sessions will support the meeting theme of energy and the environment and will feature preeminent speakers and panelists. Sessions and session chairmen are as follows:

1. *Global Environmental Effects: The Carbon Dioxide Problem From an Energy Policy Perspective*, Chairman: Robert T. Jaske, 7908 Chelton Road, Bethesda, MD 20814.
2. *Global Environmental Effects: Acid Rain*, Chairman: Dr. A. H. Johannes, Rensselaer Polytechnic Institute, Troy, NY 12181.
3. *1983 Clean Air Act Amendments: Ramifications for Process Change in the Chemical/Petrochemical Industry*, Chairman: Dr. Richard D. Siegel, Stone & Webster Engineering Corporation, P.O. Box 2325, Boston, MA 02107.
4. *Gaseous and Particulate Fugitive Emissions*, Chairman: Dr. L. Forney, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332.

Please contact the respective session chairman if you are interested in contributing to any of these sessions. We expect that symposia will be cosponsored by both the Air Pollution Control Association and the American Meteorological Society.

Richard D. Siegel, PhD
Chairman, Air Technical Session

Air Task Force

On April 7, 1982, as part of its regulatory reform program, the Environmental Protection Agency (EPA) proposed rules and regulations for an emission trading policy. Commonly known as the "bubble policy," the fundamental concept behind the Agency's proposal is to allow a source to regulate its emissions from the entire plant, rather than from each individual emission source within the facility. The Air Task Force submitted comments to EPA on its proposed rule on July 1, 1982, drawn primarily from material prepared by its Cochairman, Mr. Jack Erdmann, of Union Carbide. The comments which were submitted are as follows:

Richard D. Siegel, PhD
Cochairman, Air Task Force

Central Docket Section (A-130)
U.S. Environmental Protection Agency
Washington, D.C. 20460

Attention: *Docket No. G-81-2*

Gentlemen:

On behalf of the Air Quality Task Force of the American Institute of Chemical Engineers, we are submitting the following commentary on the Emissions Trading Policy Statement.

The Task Force believes the Policy Statement is to be a significant forward step in air pollution abatement because of the expansion of opportunities to use technically sound, cost effective methods to achieve or even exceed regulatory goals in emission control. The Policy Statement and accompanying Technical Issues Document open up opportunities for effective control on a technical level, which is where final results are to be realized. The more engineers can apply common sense and documented facts to these problems, with a minimum of administrative and regulatory interference in the attainment of real reductions (performance oriented goals), the better our chances of making significant environmental improvements overall.

One problem with such a policy is that it can be misinterpreted by critics of industry and of the present EPA administration as a weakening or dismantling of the regulatory process, thus ostensibly allowing increased emissions and poorer environmental quality. To many of these critics, any steps which reduce the costs or degree of control which must be applied are considered "weakening" or giving "license to pollute," in spite of the facts showing that equivalent or better results could be obtained with the performance goal approach. However, application of the Policy Statement and publicity about the many examples of equal or better results for lower costs should point up the fallacy of these arguments. We suggest that EPA take steps to inform the public that this policy is *not* a weakening of pollution control efforts.

Among the major changes in the new policy is one allowing for broader use of emission reductions from process shutdowns. It makes good sense that if an individual plant can voluntarily achieve a real reduction in emissions of a particular kind to meet a State Implementation Plan requirement for a certain amount of reduction of such emissions by shutting down a process instead of spending additional funds on that or other similar emission sources, it should be able to take credit for the benefits. After all, the final result must be equal to or better than the original SIP requirement, or it wouldn't get approved. The new policy rules still make sure that the final result is directed toward ultimate attainment of the NAAQS. Those who say the plant would have been shut down anyway are obviously concerned more with the fact that the industry avoided spending additional funds, than with the reduced emissions which resulted. Thus, it appears that EPA has taken a step to separate the pollution control efforts from the politics, which is the only way to make technically sound decisions and bring about real improvements to the world we live in.

If any EPA officials would like to discuss these comments further with members of the Task Force, please let us know.

Sincerely,
Martin Siegel
Staff Director—Government Relations

AAEE/ENVIRONMENTAL DIVISION COOPERATION

Largely through the efforts of Robert T. Jaske, who is an active member of both organizations, a committee is being formed to promote close cooperation between the American Academy of Environmental Engineers and the AIChE Environmental Division. Among the goals already agreed upon are (1) co-sponsorship of speciality conferences on topics of mutual interest and (2) sponsorship of sessions by AAEE at AIChE meetings. A start has been made by arranging for the two organizations to receive each other's publications.

March 27-31, 1983
AIChE's Spring 1983 National Meeting
And 12th Petrochemical and Refining Exposition
Astrohall, Houston, Texas

Group #9: Environmental Division

Program Coordinator: Aziz A. Siddiqi, ARCO Petroleum Products Co., P.O. Box 2451, Houston, TX 77001. Tel. (713) 475-4111.

9a Air Section—Chairman: Aziz A. Siddiqi.

Advances in Fugitive Hydrocarbon Emissions—Chairman: James Kamas, Radian Corp., P.O. Box 9948, Austin, TX 78766. Tel. (512) 454-4797.

Trends in Air Pollution Monitoring—Chairman: Dr. Duane J. Johnson, Environmental Research & Technology, Inc., 6666 Harwin Dr., Suite 600, Houston, TX. 77036. Tel. (713) 977-6611.

Atmospheric Impact of Direct Coal Combustion for Power Generation—Chairman: Fred W. McGuire, Houston Lighting & Power Co., Environmental Protection Dept., P.O. Box 1700, Houston, TX 77001. Tel. (713) 486-2700.

Coal Liquefaction and Gasification—Atmospheric Impact—Chairwoman: Denise Y. Wolfs, P.E., Exxon Co., U.S.A., Synthetic Fuels Dept., P.O. Box 2180, Houston, TX 77001. Tel. (713) 656-1554.

Refining and Petrochemical Advances and Atmospheric Emission Control—Chairman: John W. Tenini, P.E., ARCO Petroleum Products Co., P.O. Box 2451, Houston, TX 77001. Tel. (713) 475-4672.

Trends in Air Pollution Regulations—Chairman: Dr. Louis "Pete" Roberts, Texas Air Control Board, 6330 Highway 290 East, Austin, TX 78723. Tel. (512) 451-5711.

9b Water Section—Chairman: Robert L. Irvine, Univ. of Notre Dame, Dept. of Civil Eng., Notre Dame, IN 46556. Tel. (219) 239-6306.

Emerging Technologies for Heavy Metal Separation—Chairman: B. M. Kim, General Electric, Corporate Research & Development, K-1 Chemical Engineering Bldg., Schenectady, NY 12301. Tel. (518) 385-8824.

International Research on Liquid Phase Oxidation of Organic Wastewaters—Chairman: Charles Hamrin, Univ. of Kentucky, Dept. of Chem. Eng., Lexington, KY 40506. Tel. (606) 258-2954.

Wastewater Management: From Source Control to Effects—Chairman: Robert L. Irvine.

Biological Waste Treatment in Chemical Industries—Chairman: Dr. John Andrews, Rice Univ., Dept. of Environmental Science & Eng., P.O. Box 1892, Houston, TX 77251. Tel. (713) 527-4092.

9c Solids Section—Chairman: Dr. Michael R. Overcash, North Carolina State Univ., P.O. Box 5906, Raleigh, NC 27650. Tel. (919) 737-2325.

Hazardous Waste Management—Chairman: Dr. Aaron Jennings, Univ. of Notre Dame, Dept. of Civil Eng., Notre Dame, IN 46556. Tel. (219) 239-5846.

Impact of RCRA on Petroleum and Petrochemical Industry—Chairman: James T. Adams, Jr., ARCO Petroleum Products Co., P.O. Box 2451, Houston, TX 77001. Tel. (713) 475-4507.

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- Three Mile Island Waste Management: A DOE Perspective.
- Radiation Effects on Ion Exchange Materials Used in Waste Management.
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Material presented was selected from papers presented at AIChE's National Meeting in Detroit, Michigan, August 16-19, 1981.

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