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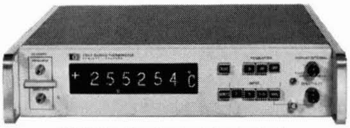

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Science & Technology

Volume 5, Number 4,
April 1971

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Diffusion of aerosols released upwind of an urban complex 327

G. R. Hilst and N. E. Bowne

The dispersive capacity of the atmosphere can be predicted to within a factor of two about 70% of the time by use of a model that was developed from a 1964–65 field study (Ft. Wayne, Ind.). The input data required are: the release position, the source strength, the wind speed at release height, and the stability in the lower 61 m of the rural atmosphere.

Oxidation of n-butane by the photolysis of NO_2 333

J. J. Bufalini, B. W. Gay, and S. L. Kopczynski

The saturated hydrocarbon, n-butane, is low on the reactivity scale but which nevertheless, in the presence of light and NO, contributes to the production of oxidants. Hydroxyl radicals are postulated as the principal chain-propagating free radicals; the presence of CO increases the rate of NO oxidation.

A simple, rapid method for determining trace mercury in fish via neutron activation analysis 336

J. M. Rottschafer, J. D. Jones, and H. B. Mark, Jr.

In the 0.05–10 ppm range, mercury in fish tissue is separated on an $HgCl_4^{2-}$ complex of an anion-exchange resin and counted directly on the resin. Analyses show a 10% standard deviation and a sensitivity of 3 ppb. The mercury content in fish from various geographical locations ranged from a low of 0.05–0.15 ppm for white fish (northern Lake Huron) to a high of 1.56 ppm for walleyed pike (Lake St. Clair, Mich.).

Tritium loss from water exposed to the atmosphere 338

J. H. Horton, J. C. Corey, and R. M. Wallace

Waste streams containing tritium can be managed successfully by knowledge of small quantities of the radioisotope as HTO found in much of the processes waters used in certain nuclear facilities. Results of the 3-year study indicate that basins should be used to transfer tritium to the atmosphere, rather than release to streams, or the like; in many cases, tritium diverted to the atmosphere will result in reduced radiation exposure to the public.

Atmospheric technetium-99 344

M. Attrep, J. A. Enochs, and L. D. Broz

Technetium-99 is becoming widespread both in the atmosphere and in the natural water system and causes concern since the material as the pertechnetate ion behaves like iodide with respect to the thyroid system. The concentration of Tc from 13 samples of rainwater taken at Commerce, Tex., in 1967 ranged from $0.14–1.7 \times 10^{-2}$ pCi/liter; these activities of Tc are low, appear negligible, and represent no major environmental contamination.

Ultrafiltration for the control of recycled solids in a biological system 345

F. W. Hardt, J. C. Young, L. S. Clesceri, and D. R. Washington

Ultrafiltration may become an integral part of future biological waste treatment systems. Industrial wastes can be treated biologically in a high-solids microbial system which contains from 20–30 grams/liter volatile suspended solids. Via low pressure ultrafiltration, the system maintains 75–95% reduction of chemical oxygen demand; the overall COD removal efficiency of the high-solids ultrafiltration system exceeded 98% at a flux rate of 4.5 gpd/ft^2.

Alkaline scale abatement by carbon dioxide injection 350

R. D. Ellis, J. Glater, and J. W. McCutchan

Scale deposits on heat transfer surfaces of distillation equipment can be eliminated by continuous injection of carbon dioxide. This injection offers certain advantages over currently used techniques for controlling alkaline scale, such as injection of acids or polyphosphate-based additives. Techniques are discussed for both the CO_2 injection and monitoring of the CO_2 concentration in a pressurized system.

Communications

Continuous monitoring of water surfaces for oil films by reflectance measurements 356

A. D. Goolsby

A simple and sensitive analyzer is available for monitoring oil slicks. Hallikainen Instrument Co. (Richmond, Calif.) has been licensed by Shell Development Co. to manufacture the monitor. The present model is suitable for still waters and refinery effluent streams; modifications are being made so that the monitor can be used under adverse sea conditions.

Analysis of barium sulfate by atomic absorption 358

M. Magyar, J. L. Bove, B. Nathanson, S. Siebenberg, and E. F. Ferrand

The total airborne barium collected in high-volume samples can now be analyzed by a simple, yet novel, method by use of atomic absorption spectrometry. The method utilizes the reducing potential of filter paper on barium sulfate which is quantitatively reduced to acid soluble barium sulfide. Formerly, barium analyses were performed by emission spectrometry which required not only expensive equipment but highly trained manpower.

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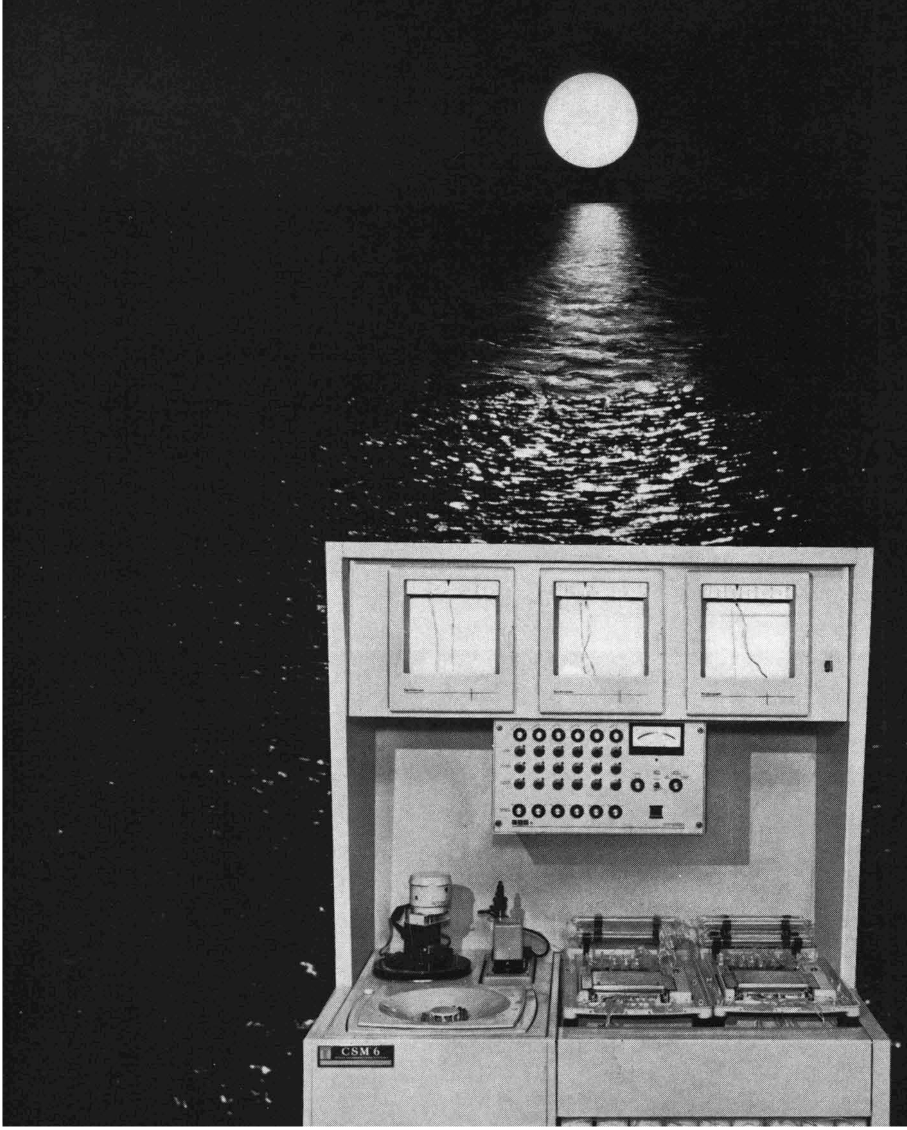

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Nitrate & Nitrite	0-2.0
Nitrite	0-1.5
Orthophosphate	0-10
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Chromium	0-5
Copper	0-10
Iron	0-10
Methyl Orange Alkalinity	0-500
Thymol Blue	0-100
Hardness	0-300
Sulfate	0-500
Phenol	0-5
Cyanide	0-3
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Color	0-250 units
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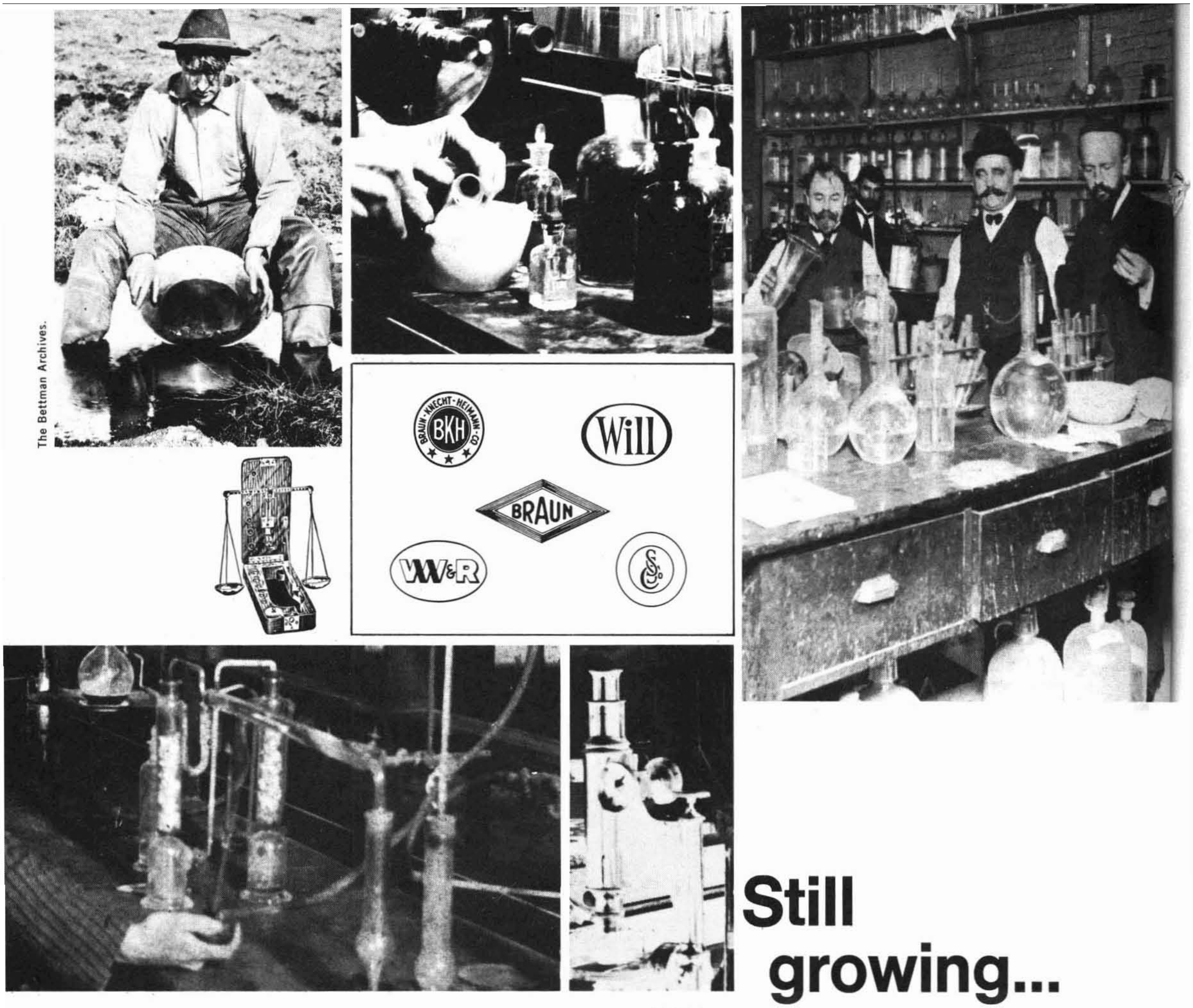
Fluoride	0-2.5
Silicate	0-15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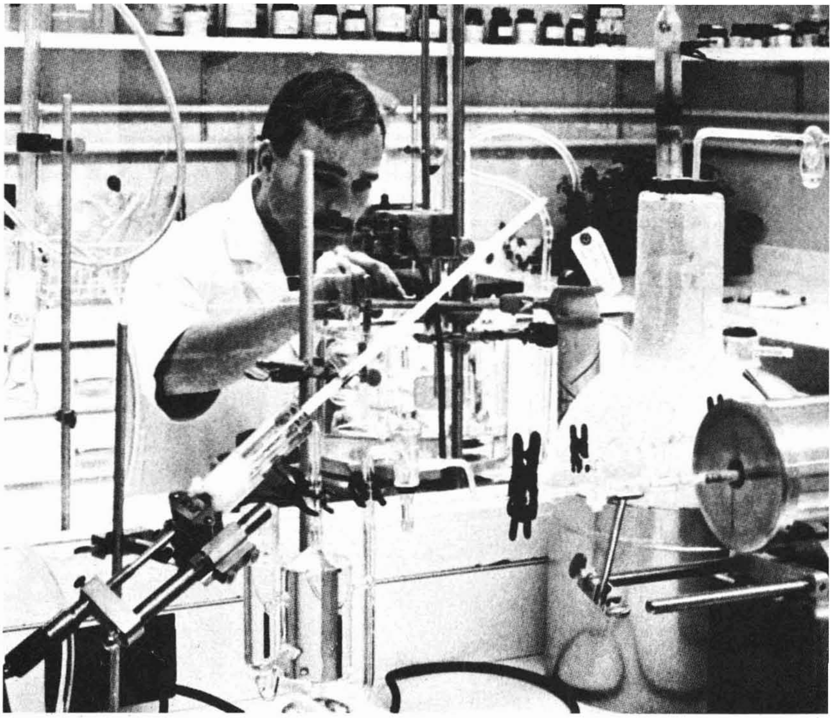

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Challenging the flush toilet

● *The Viewpoint by Harold H. Leich in our January issue (page 11), "A challenge to the environment pro," resulted in more than 50 letters from readers. A representative, edited selection follows.*

DEAR SIR:

Mr. Leich's question: "Can modern technology devise a better method of sewage disposal . . .?" is certainly answered "yes." It is unnecessary to use scarce and expensive drinking water for this purpose, as it is much more appropriate to use reclaimed waste water or polluted surface waters, conserving high-quality drinking water for high-quality uses.

Water is plentiful if we manage it properly; it is one of our renewable resources. To cease using it for essential functions is a retrograde step . . . .

Many proposals have been made for individual household reclamation systems. However, any cost analysis would show that such systems are far more expensive than community water reclamation systems.

Daniel A. Okun
Environmental Engineering Dept.
University of North Carolina
Chapel Hill, N.C. 27514

DEAR SIR:

My answer to Mr. Leich's question is "yes." Not only has such a method already been developed beyond the conceptual stage, but it is not too far removed from Mr. Leich's proposed system. The solution is embodied in Environmental Sciences' Chemfix process.

The Chemfix process, which is presently being used for ultimate disposal of industrial sludges and concentrated liquid waste, consists of chemical detoxification, deodorization, and solidification. The solidified human waste so produced can ultimately be buried in a landfill or incinerated. It is biologically harmless, nearly odorless and mechanically stable.

J. R. Conner, president
Environmental Sciences, Inc.
Pittsburgh, Pa. 15226

DEAR SIR:

Mr. Leich's degradable canister could possibly be made of asphalt-coated paper. We are testing this material as a mulching material; it is waterproof and biodegradable. As for the powder, hydrated lime has been used for years to aid in decomposition and reduce odors of animal wastes. A paper canister containing sewage and hydrated lime could be incorporated into the topsoil with conventional farm equipment, probably annually.

F. M. Rhoads
College of Agriculture
University of Florida
Quincy, Fla. 32351

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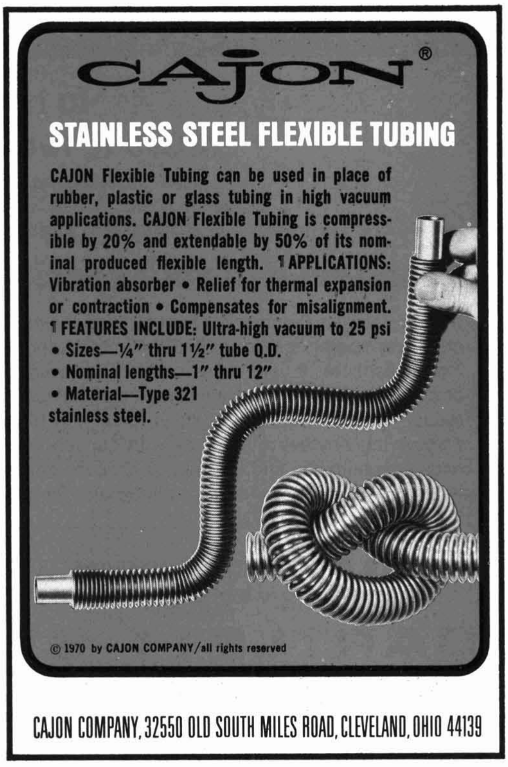

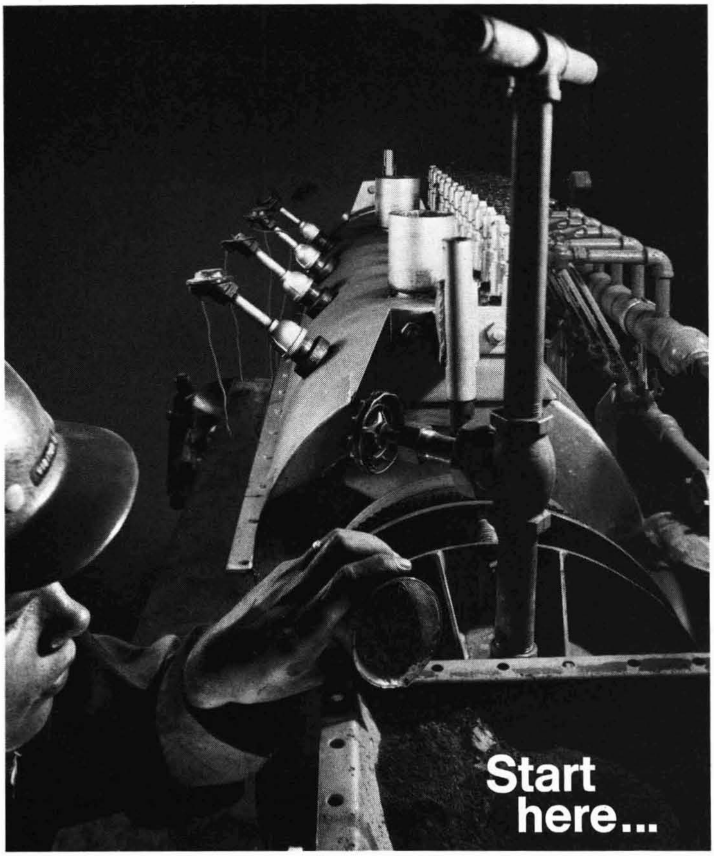

(continued from page 281)

DEAR SIR:

Mr. Leich's article should get the prize for the most "far out" thinking yet. You are actually suggesting we go back to the days of the outhouse. This system is used in the Orient where "honey wagons" empty the waste and haul it out to village farmers.

In this town, you are lucky if the garbage man can get round to picking up your garbage. Can you imagine bags of human waste sitting for days waiting for a pickup?

Edward E. Potenza
P. O. Box 4044
Sarasota, Fla. 33578

● *Mr. Potenza's sentiments were echoed by several others—Ed.*

DEAR SIR:

We were surprised that no one had mentioned the electric toilet and the gas toilet as alternatives to the flush toilet. It is our belief that your readers will be equally interested in the ecological advantages of these alternatives.

Newton A. Brokaw
7309 McNear Court
Peoria, Ill. 61614

DEAR SIR:

I have learned that LaMere Industries, Inc. (Walworth, Wis.) manufactures commercially a toilet called Destroilet. This is a self-contained unit designed for use on boats and campers, but could easily be adapted for home use. In this unit the human excrement is collected and immediately burned with propane gas. Retail cost is presently about $350, plus gas and electricity expense. This certainly satisfies the general requirements of no more water supply contamination and elimination of disease-spreading problems and odors connected with reducing the organic content of urine and feces.

Keith H. Steinkraus
Microbiology Dept.
Cornell University
Geneva, N.Y. 14456

● *Several other readers also brought the Destroilet and similar units to our attention—Ed.*

DEAR SIR:

I suggest that where sewer lines are going to be installed in an area now using septic tanks, only "gray

(continued on page 287)

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(*continued from page 282*)

sewage" (kitchen, laundry, and bath wastes) be connected into the line. With so many houses equipped with automatic clothes and dishwashers, plus the American penchant for frequent bathing, by far the greater volume of sewage entering septic systems is "gray sewage." Septic tanks left to handle "night soil" only should be able to handle the job indefinitely.

Daniel P. Dash
113 Killarney Rd.
Knoxville, Tenn. 37919

DEAR SIR:

Unfortunately, your sincerity and enthusiasm are matched by your naiveté on the subject of "strong-smelling chemical toilets." If you have traveled on any commercial jet airliner in the past ten years, the toilet facility was undoubtedly a recirculating chemical toilet. Yet, I am sure that it was certainly not offensive to any of your senses. Most such modern toilets use only an initial charge of four gallons of water and an effective deodorant. The rest of the fluid used to flush with is a diluted, filtered urine solution.

Nathan J. Krotinger, president
Zevel Corp.
La Mirada, Calif. 90638

● *Several makers and users of chemical toilets have sent us favorable comments on use of these units—Ed.*

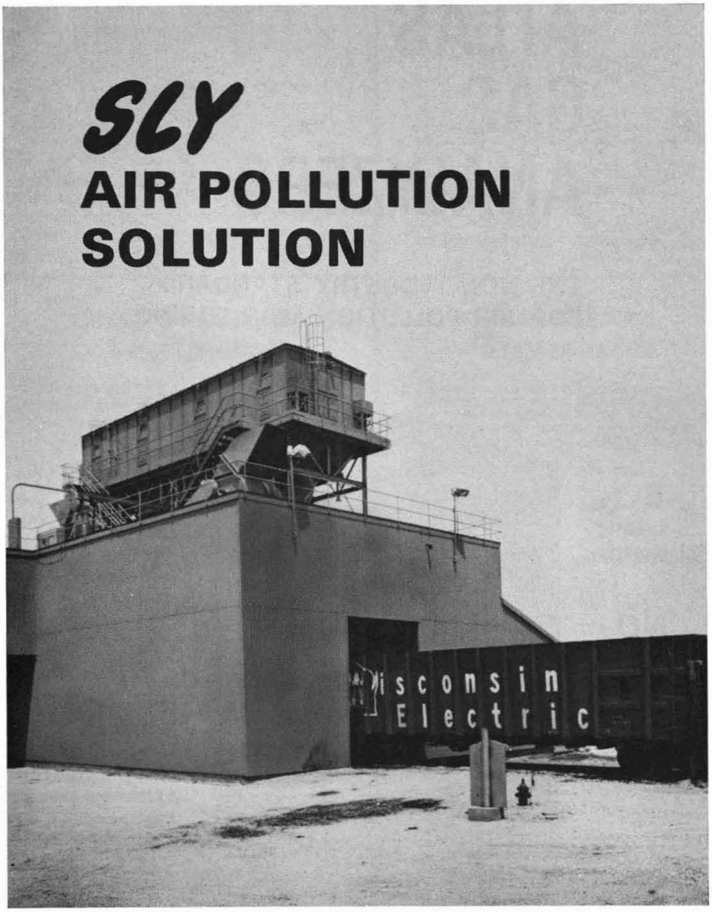
DEAR SIR:

In order to determine whether research funds might have been available to study the concept raised in Mr. Leich's Viewpoint, I contacted two federal agencies in September 1970. Their responses were negative. One stated that "it has been suggested many times" and emphasized that handling, hauling, and final disposal were the unsolved problems in this area. The other's response was that "limited research funds and program priorities" prevented their consideration of the concept.

Perhaps a coordinated approach to environmental research by EPA will include further studies on elimination of problems as well as treatment of problems.

William J. Jewell
Dept. of Civil Engineering
University of Vermont
Burlington, Vt. 05401

(*continued on page 288*)



(continued from page 287)

Phosphate removal process

Dear Sir:

We would like to call attention to two aspects of the Environmental Currents item on the PhoStrip phosphate removal process published in your January 1971 issue, page 15.

The diagram you prepared does not provide for sludge return from the anaerobic tank to the aeration basin. Sludge return is an essential part of the overall process, as it is of the activated sludge process itself. The text refers to phosphate being concentrated in "an anaerobic digestion process." The step in which the phosphate taken up by the microorganisms is released is not digestion but merely the imposition of anaerobic conditions for a brief period, to induce the living organisms to release phosphate. Finally, if the process centers on any step, it is not the "higher-than-normal aeration rate" cited, but, we think, the cycling of the microorganisms through the anaerobic tank.

Gilbert V. Levin, president
Biospherics Inc.
Rockville, Md. 20853

Joseph Shapiro
Limnological Research Center
University of Minnesota
Minneapolis, Minn. 55455

Unobtainable insurance

Dear Sir:

In the article, "Is pollution insurable?" that appears on page 1103 of your December 1970 issue, you report on the exclusion endorsement which the insurance companies of America have added to all of their liability insurance policies outstanding. We would like to point out that this is not the only type of exclusion the insurance companies have made in regard to their potential liability involving pollution suits.

Enviro-Trol, Inc. was formed last year to help industries solve their pollution problems. Since we are offering both a testing and consulting service, we feel the need for professional liability insurance. However, even though we are owned by a much larger company with considerable insurance coverage, liability insurance has so far been denied our operation. We are for the time being operating without this coverage, but it is very risky business to say the least.

It seems to us that something has indeed gone awry when a firm that was established to aid and solve one of our most pressing problems cannot get adequate insurance. We, of course, are hopeful that this situation will change in the near future. In the meantime, if other readers can find a solution to this, we will appreciate hearing from them.

Charles W. Dean, president
Enviro-Trol, Inc.
Memphis, Tenn. 38112

A pound's a pound, for a' that

DEAR SIR:

The article entitled "Fuels management in an environmental age," by Mills, Johnson, and Perry (ES&T, January 1971, page 30) contains two similar statements which, when juxtaposed as they are, can create a misconception. We find the following, which can be accepted as authoritative and meaningful: "About 95% of all sulfur oxides, 85% of all nitrogen oxides, and over half of the carbon monoxide, hydrocarbons, and particulate matter are produced by fuel use." I have no quarrel with this statement.

But immediately preceding it we find this: "Nearly 80% of all air pollution in the U.S. is caused by fuel combustion." This kind of statement gains stature by being put alongside the first, yet it is patent nonsense. Only if fuel combustion were responsible for 80% of the emissions of each and every pollutant (which the other statement belies) or if all pollutants were equally hazardous and economically damaging (which cannot be) would the statement stand up. It is based on the premise that, as Robert Burns might have said, 'A pound's a pound for a' that.' Is a pound of carbon monoxide to be weighed with a pound of cement dust, a pound of chlorine, a pound of benzpyrene, or a pound of nerve gas?

The authors have not, at least, used this empty argument as a smokescreen to hide the sins of an industry. Beware the pious manufacturer who says, "Our industry causes only 0.2% of all the air pollution in the country. Why pick on us?"

David B. Marsland
Dept. of Chemical Engineering
North Carolina State University
Raleigh, N.C. 27607

New anti-fouling pH electrodes:

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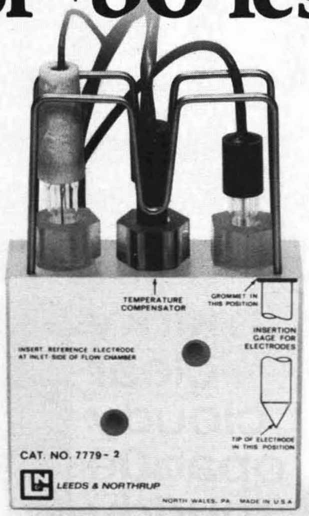

Bad enough, you've had to put up with the aggravation of trying to get a pH reading out of some messy gunk.

Worse, you've had to pay for the privilege: $125, usually, for just the oversized reference electrode needed to cope with the crud. But what could you do? It was either that or pay about $365 for some over-engineered whiz-bang.

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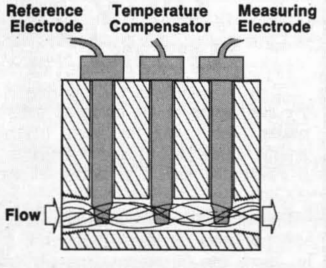
Now we can give you a foul-fighting reference electrode for $45. Standard size. Standard shape. Ready for use in L&N mountings or, with some judicious grommeting, in anybody else's mounting.

Or you can get our new electrode in our new self-scouring mounting shown above. And not for $365 either. For $185—complete.

It works. Beautifully. Everywhere people try it. In a 20% oil-in-water emulsion, for instance. After six months, our new electrode was still going strong. Without failure. Without signal degradation. With nothing more than an occasional, routine, inspection.



Another customer was faced with a contaminant so vile that 6 ppm drove him, and his pH recorder, up the wall. We tested our new electrode in a 200 ppm environment—33 times worse—with complete success.

The electrodes work best when set up as we've shown here: with the reference electrode upstream of the sensing electrode and temperature compensator. This way the flow helps scrub the gunk from the reference electrode tip.

You don't have to do it this way, though, because stream scrubbing is only one of our anti-fouling tactics. The major part of the job is done by the tip of the reference electrode itself. It's new: a permeable ceramic plug that provides thousands of KCl outlets, not just one, easily clogged, path.

There are some other engineering niceties about our new pH electrodes that make them ideally suited for less-than-ideal liquids. The information's in L&N data sheet D2.1117TP. Write for a copy.

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editorial

Planning for land use is imperative

The critical shortage of land for waste disposal sites emphasizes the inadequacies of random land development

Nothing makes Homo sapiens look more like some sort of giant ant than his frantic grubbing around for places to deposit his accumulated solid wastes. And few things point up the inadequacy of his public institutions, at least in the U.S., more than the institutionalized barriers that prevent him from locating disposal sites in accordance with any sort of rational plan.

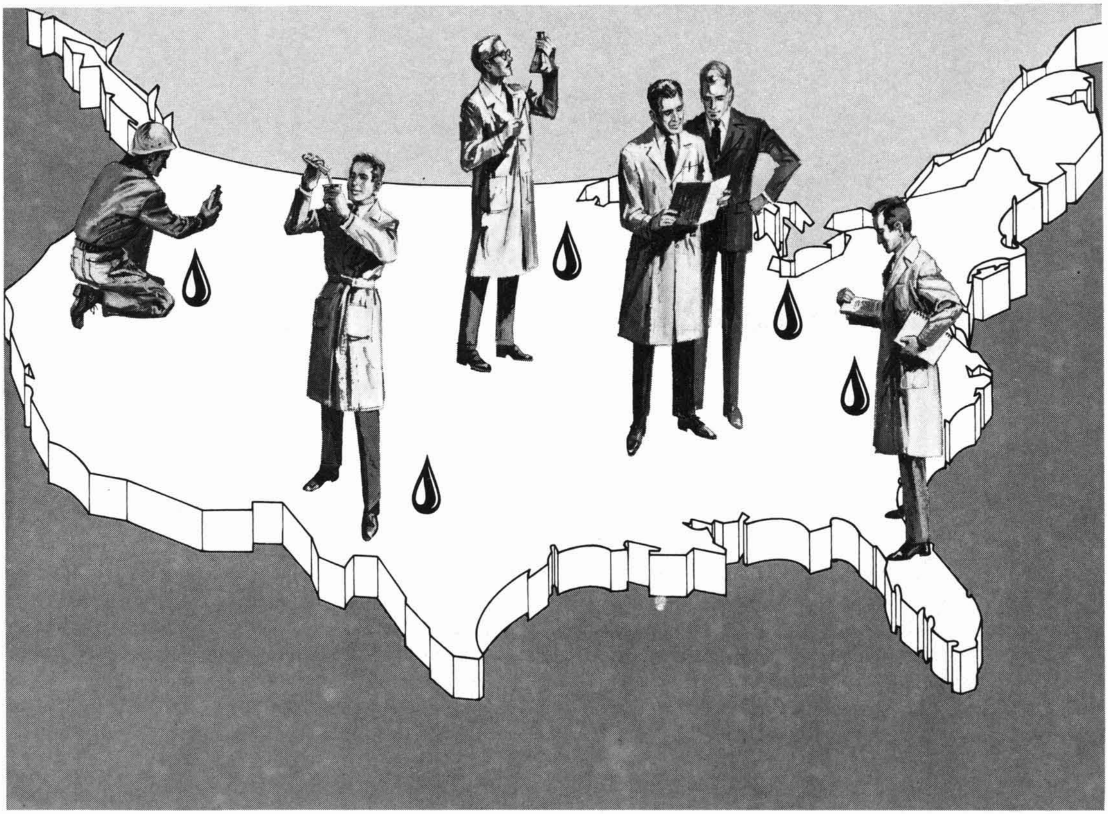
Several basic facts emerged recently at a symposium on solid waste disposal sites sponsored by the American Public Works Association. First, most solid wastes in this country are disposed of directly into the land. Second, the great majority of land disposal sites is grossly inadequate from the public health standpoint (94% of 6000 sites sampled by the federal Solid Wastes Management Office did not meet "even the most modest criteria" defining a sanitary landfill). Third, most urban areas have run out of space in their own jurisdictions and are experiencing great difficulty in finding sites outside their boundaries. Further, there is a disturbing trend toward restrictive local zoning which excludes landfill sites from many small jurisdictions that otherwise could accommodate them. In essence, everyone produces solid waste but no one wants it disposed of anywhere near where he lives (an understandable reaction in view of the health menace posed by existing sites). Since people live practically everywhere, this brings us to some sort of an impasse.

Current alternatives to direct land disposal are really only partial solutions to the problem, since they usually give rise to large quantities of residual solids that still have to be disposed of somehow. The residue from incineration, for instance, amounts to over 50% of the solids "burned." Since widespread recycling is still some years away, despite the intensity and sincerity of current efforts in that direction, there remains a critical need to find land disposal sites that are both sanitary and acceptable to the public at large. The situation has public officials up against the wall. SWMO has estimated that, on the average, existing sites will last only another 4–5 years. Many officials at the APWA symposium reported that their sites have just a year or so left, and they have been unable to acquire land for future use. The situation is so desperate, indeed, that some municipalities have been forced to violate their own zoning ordinances in order to obtain a site.

Assuming we are all in agreement that there is a problem—what can we do about it? It seems to us that the paramount need is for land use planning at a level above that of local government. The state level would be a good place to start. On the specific subject of waste disposal sites, not all land is suitable (by virtue of a high water table, for example), and it seems logical that a state should designate suitable areas for use only as landfill sites. Hopefully, a state would be more immune to land developer pressure than smaller jurisdictions have proved to be.

While the concepts of air quality and water quality are fairly well established and lie at the heart of remedial measures designed to assure clean air and water, land quality and land management are fairly new concepts in the environmental field. A recognition of the need to plan land use and the establishment of workable mechanisms to do it are imperatives right now. For until such a time as we can reach the goal of complete recycling of solid wastes—a goal which ES&T embraces as firmly as anybody—it is only prudent that we face the facts of life and work out rational plans for disposing of the wastes that we have not yet had the intelligence or foresight to reuse.

D. H. Michael Bowen



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Circle No. 13 on Readers' Service Card

viewpoint

Richard D. Vaughan

Acting Commissioner, Solid Wastes Management Office
Environmental Protection Agency

Solid waste management—everybody's problem

Until quite recently, one could accurately refer to solid waste management as America's forgotten problem. It was usually at the bottom of a city's priority list of things to do. The philosophy seemed to be—why worry about garbage until it piles up around your door?

Then, suddenly things began to change. With the advent of the garbage strike, our citizenry was given a taste of what life would be like without collection service. Pollution control authorities began demanding an end to incineration in overloaded and outmoded facilities that were often without even a pretense of air-cleaning equipment. Others spoke out against a major insult to our environment—the open burning dump. The few good disposal operations began facing a dilemma when land available for sanitary landfills became scarce or too expensive. The careless American littered his countryside with reckless abandon and then complained when his taxes went up to collect his trash. About that time another type of citizen came along who said he was concerned about the "solid waste problem" but strenuously objected to any solution, or disposal site, located near his part of town. He didn't seem to care that the facility had to be in someone's part of town.

Who caused all this? Everybody! There is an increasing number of us, and in our affluent way we produce more and more waste per person. We are not handling our present waste load adequately, and prediction calls for doubling this amount long before we leave the twentieth century. Thus, the proper management of this nation's solid waste is everybody's problem.

If it is truly everybody's problem, then everyone should work toward a realistic solution. What can we do?

- The scientist can turn his genius toward developing better technology to handle this problem.
- The economist can devise more equitable ways to raise money for the necessary task of management in such a way that a major part of the cost is borne by those who cause the problem.
- Personnel charged with enforcement can vigorously pursue their responsibility of making people obey the law in the environmental pollution control field, much as they are required to obey the law in other areas.
- The municipal official can accept solid waste management as high priority responsibility. He can demonstrate his concern by eliminating open dumps and other unsatisfactory practices, and replacing them with practices that protect rather than degrade our environment—even if it costs more money.
- The industrialist can ensure that all wastes from his plant are managed properly and recycled wherever possible. He can also give thoughtful consideration to the effect on the environment when he develops new products which tax the nation's solid waste management capabilities.
- The educator can help instill in our country's citizens a concern for the preservation of our environment. This concern should be important to our youth as well as our adult citizens.
- The concerned citizen can perhaps play the most important role of all by insisting that those responsible for solid waste management in his community do a good job now and adequately plan to ensure that a good job will be done in the years to come. Mr. and Mrs. Citizen can also voice their displeasure to those industries that do not handle their own wastes properly, or continue to develop products without concern about their environmental effect.

Because effective solid waste management is everyone's problem, it is everyone's business to help solve the problem.

Richard D. Vaughan is the Acting Commissioner of the new EPA*'s Solid Wastes Management Office. He was formerly the Director of the Bureau of Solid Wastes Management under* HEW

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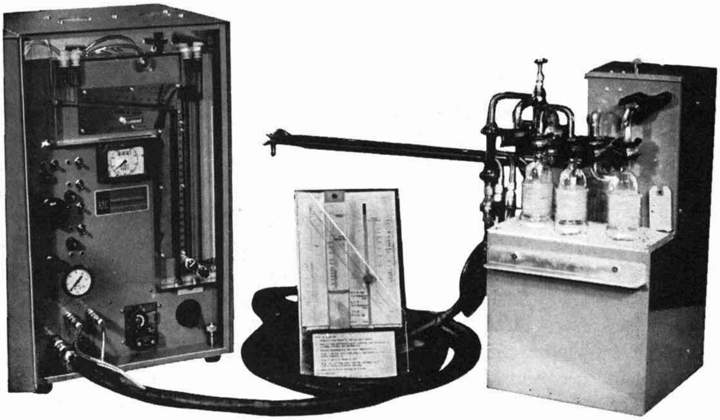

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CEQ revises guidelines for environmental statements

The Council on Environmental Quality has added a major change to its guidelines calling for earlier availability of statements to the public. The revision specifies that draft statements on administrative actions by agencies should be released to the public as soon as they are circulated for comment. No action is to be taken for at least 90 days after public availability of the statements. The revised guidelines also call for public hearings where appropriate. The environmental impact statements are required by the National Environmental Policy Act of 1969. By the end of February, 380 environmental statements had been submitted.

DOD suspends ocean dumping of old munitions


Defense Secretary Laird

The U.S. Navy had planned to dump 103,777 tons of ammunition in the ocean in 1971 and another 80,000 tons in 1972. But, recently Defense Secretary Melvin R. Laird suspended such disposal practices. In recent hearings of the Senate Commerce Subcommittee on Oceans and the Atmosphere, Navy Secretary John H. Chafee said that the munitions were not of critical shelf life now and that the Navy is looking for other disposal methods.

EPA meets another four air pollution deadlines

By the end of last month, the Environmental Protection Agency had met its deadlines for: • Publication of hazardous air pollutants including asbestos; • Proposed performance standards for stationary sources including power plants, municipal incinerators, cement plants, sulfuric acid plants, and nitric acid plants; • Announcement of the aircraft emissions study; and • Complete designation of federal air quality control regions. A total of 235 regions was designated which covers the bulk of the country. Also, last month EPA published its list of '71 model year, light-duty vehicles which have been certified to meet the 1971 federal emissions standards. The certifications cover 90 engine classifications used in 400 model vehicles from nine domestic and 28 foreign automobile manufacturers.

Patent Office: first-year results of priority program

Since Feb. 10, 1970, when the accelerated processing of environmental patent applications was announced, 380 applications have been given the accelerated processing status. "Of the 380 priority applications, 78 have already been approved by patent examiners for patent issuance," says William E. Schuyler, Jr., commissioner of patents (ES&T, November 1970, page 895). "Over 700 patents which related to the environment actually have been issued during the past year."

NSF funds undergraduates and gets new research group


NSF's Eggers

Under a National Science Foundation grant totaling almost $1.5 million, more than 1100 college students will spend their summer this year performing environmental research. As part of the agency's SOS (Student Originated Studies) program, each project is carried out under the leadership of one of the students who serve as student project director; a group consists of from 5–21 studies at one of 97 colleges or universities. Dr. Alfred J. Eggers, Jr., assistant director for research applications, heads a new NSF unit to support research aimed at environmental, societal, and technological problems, under Project RANN (Research Applied to National Needs).

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A specially designed permeation tube calibration system (above) assures the accuracy of analyses. An industry standard, it has been characterized as "the only permeation system that really works."

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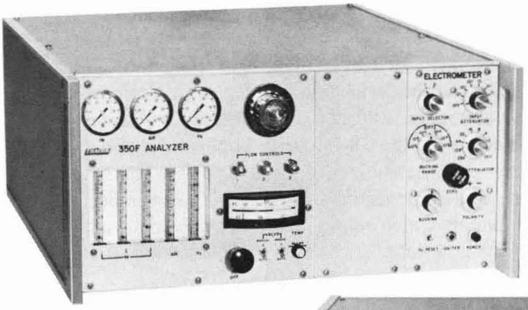

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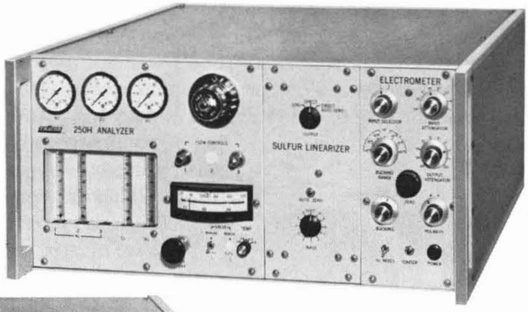

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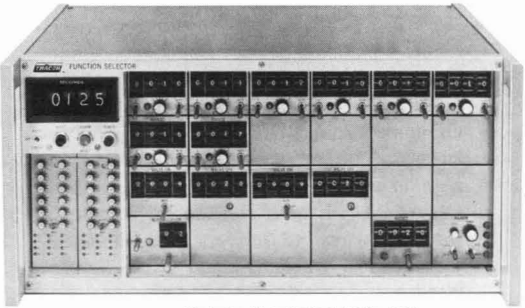

AUTOMATIC FUNCTION SELECTOR

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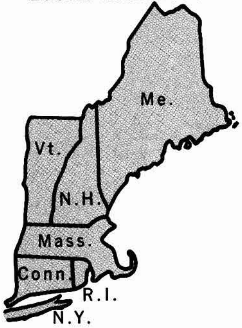
environmental currents

STATES

In New England state, federal actions are combined



New England River Basins Commission

The New England River Basins Commission, established by President Lyndon B. Johnson in 1967 under the authority of the Water Resources Planning Act of 1965, begins its fourth year of operation. Future planning calls for more integration of state and federal water and land resource programs based on state boundaries as well as basins. The 7-state commission—Connecticut, Maine, Massachusetts, New Hampshire, New York, Rhode Island, and Vermont—has begun developing a management program for the rivers and coastal areas of eastern Massachusetts and Rhode Island and is seeking funds to study Long Island Sound. The accomplishments and future plans show the partnership of state and federal agencies effectively working together.

Georgia issues air pollution notice to Atlanta

The city of Atlanta was given 45 days (ending this month) to submit a plan of action to correct air pollution emissions from its two incinerators or face "further legal action" by the Georgia Department of Public Health. Emissions from Atlanta's two incinerators violate the state's air quality rules. If appropriate plans for effective emission controls are not presented by the deadline, the health department will issue an official cease and desist order. One incinerator in question produces 234% more fly ash than is permissible. The other incinerator does not even meet the state's standards on visible smoke emissions.

Mich. removes phosphorus; Tenn. wants law change

The Michigan Water Resources Commission reports that removing 90% or more phosphorus from municipal wastes is possible through careful regulation of chemical feed rates to the waste water flow through treatment plants. Furthermore, in 1966, the commission was the first pollution control agency in the U.S. to establish 80% phosphorus removal requirements for waste treatment plants. Ten major changes to the Tennessee Stream Pollution Control Act have been suggested. Considerations include establishing effluent permits under law; stringent penalties for pollution violators; tolerance limits, permits, and action against polluters in the hands of the Public Health Commissioner; and closer contact between the Stream Pollution Control Board and Tennessee citizens.

Florida, Connecticut handle solid waste problems

Orange County, Fla., is designing and building a sanitary landfill that will not pollute the groundwater in spite of the high water table in the area. The demonstration landfill will be permanently dewatered, by use of drainage channels, so that the water table will be forced below the level of the refuse cells to be constructed. This EPA-assisted project will replace nine dumps scattered throughout the county. This summer, the city of Milford, Conn., plans to open its new $1.9 million solid waste disposal plant, the first municipally funded facility of its kind in the U.S. The plant combines the use of shredders with sanitary landfill operations; the combination is believed to be one of the major breakthroughs in landfill operations in recent years.

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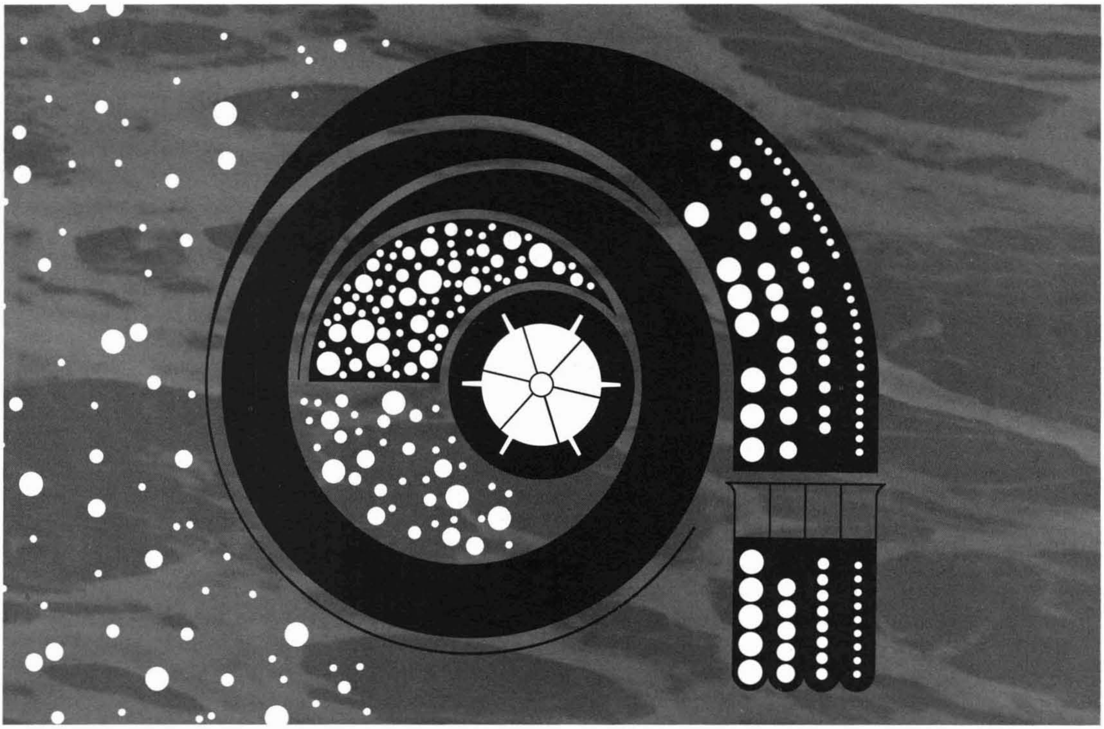

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STATES

New organizational structures take hold

Nine state governments have revamped their structures to improve their management of the environment. The interdisciplinary approach gives fresh impetus to existing environmental programs and state organizations by combining institutional design with legal and environmental analysis. A final report, available this month from the Woodrow Wilson International Center for Scholars (Washington, D.C.) describes these new organizations: • Consolidated environmental departments (New York, Wisconsin, Washington, Minnesota, Illinois); • Land use management agencies (Vermont, Maine); • A waste management agency (Maryland); • State courts, given a new role in environmental protection through public interest law suits by private citizens (Michigan).

TECHNOLOGY

Electrostatic coating system cuts pollution

Farboil, a division of Beatrice Foods, has developed a single-application, dry coating system which the company says gives a durable, laminated finish to metal surfaces and is "absolutely pollution-free." The powder mixture—a combination of zinc, epoxy, and one of several plastic polymers—is applied electrostatically with an air gun to negatively charged metal objects such as automobile parts. The rate of application and electrostatic charge pickup differential results in a laminar finish after heat curing. Zinc forms a rust-resistant primer coat, epoxy adds durability, and the plastic finish coat provides resistance to chemicals. No solvent is used and overspray is easily reclaimed, eliminating air and water pollution.

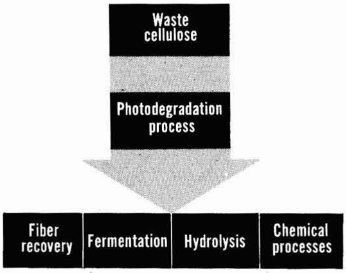
Sewage sludge yields high protein animal food

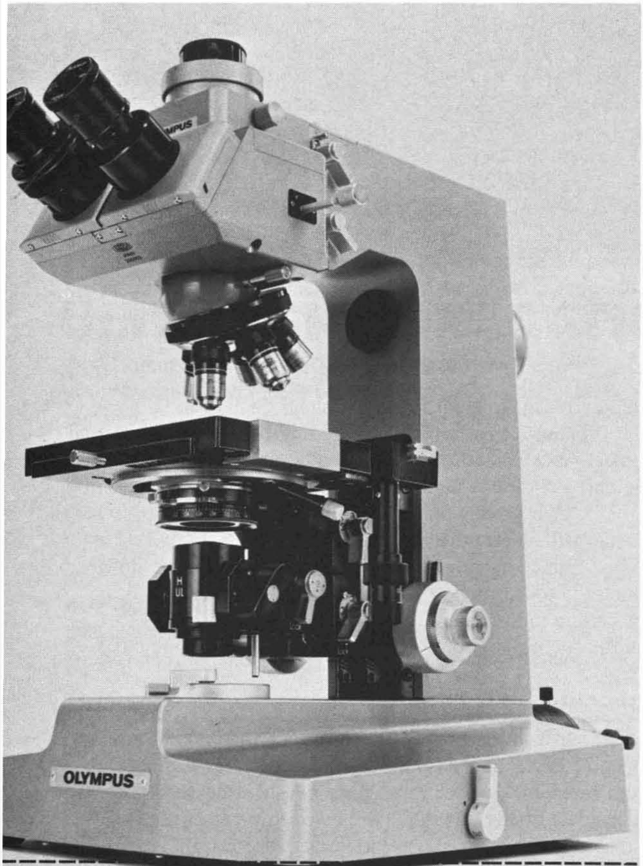
Primary sewage sludge from municipal waste treatment plants can be converted to a high protein, fat-free animal food using technology developed by Alpine Geophysical Associates, Inc. The dual extraction process uses ethylene dichloride and isopropyl alcohol to rid sludge of fats and water. The solid fraction has a high protein efficiency ratio in test feedings with laboratory animals and will be suitable as food for chickens, fish, and shellfish. The oily by-product fraction could be used as fuel to drive down the cost of processing the solid fraction. The liquid fraction may also be a valuable pool for certain industrial and pharmaceutical compounds. Sludge protein concentrate costs about 6 cents per pound to manufacture.

Degradation of cellulose is under study

The Gillette Co. Research Institute (GCRI) has signed a $50,000 contract with the Environmental Protection Agency to study the recycling of cellulose waste from municipal, agricultural, and industrial processes. Only token support will be given by EPA; $49,000 will be contributed by GCRI. Specifically, the process under study is an accelerated photodegradation reaction which reduces the degree of polymerization of waste cellulose. Cellulose is treated with one of several inorganic salts, such as sodium nitrite, and is exposed to ultraviolet light which depolymerizes the cellulose molecules into smaller units. Once in this form, the waste cellulose can be more readily converted into useful products, such as alcohol, antibiotics, or food-grade yeasts.

Cellulose utilization

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RELATIVE SIGNAL STRENGTH
CHANNEL 1
CHANNEL 2

INDUSTRY

Big growth predicted for air pollution instruments

Arthur D. Little, Inc. has just completed a study of the markets for air pollution analysis instrumentation for both stationary and mobile sources. The study appears to be in broad agreement with a previous similar one by Esso Research & Engineering Co. (ES&T, August 1970, page 639). Although full details are not available (the study report is obtainable only by paying $4000) an A.D. Little spokesman reveals that the segments likely to grow fastest are those involving stationary source monitoring and auto exhaust measurement. The market for ambient air instruments will level off fairly soon, says the spokesman; the Esso study predicted that this segment will peak in 1972 and decline thereafter. Little reportedly agrees with a figure of $500 million as the probable total size of the market in the period 1970–80.

Pollution control executive: new breed of cat

The trend toward establishment of special pollution control groups in industrial companies is continuing. Eighty-nine of 174 "pollution-prone" North American firms recently polled by The Conference Board, a New York City-based research organization, have set up such groups at the corporate level. The Conference Board reports in its publication "Corporate Organization for Pollution Control" that the average pollution control executive has an engineering degree and may exert considerable influence over major policy decisions in addition to his main job of implementing pollution control programs.

Federal government erodes state antipollution authority


Georgia-Pacific's Gould

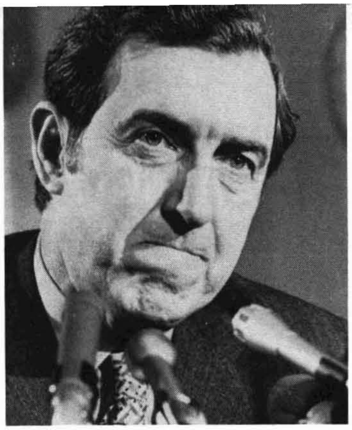
The increased federal presence in the pollution control picture is coming in for some sharp criticism. Matthew Gould, environmental protection director for Georgia-Pacific Corp., has attacked what he sees as a lack of effective decentralization in the federal structure and a continuing civil war between federal and state agencies. Gould fears imminent erosion of state authority in the face of increased and impersonal federal involvement. At the same time, industrial representatives seem more eager than ever to have pollution laws rationalized. Earle S. Ebers, president of Uniroyal Development Co., told a Missouri symposium that he believes there is a clear need for better coordinated regulatory policies. "If, as a businessman, I want to set up a chemical plant in Ohio to make the product I am now making in Louisiana, why shouldn't my new plant be subject to the same environmental criteria?" he asked.

Group looks for industries compatible with environment

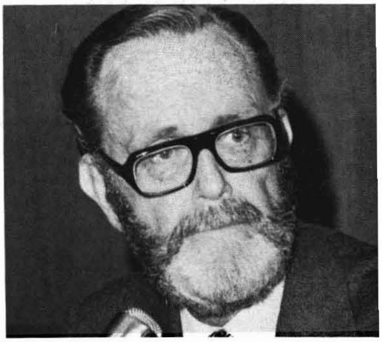
The University of Utah has instituted a program that will attempt to find ways in which the state's natural resources can be developed in a manner consistent with environmental protection. Robert G. Larsen, director of the university's new Center for Environmental Studies tells ES&T that the objective of the center is to bring the talents of the university to the solution of community problems. Larsen will direct programs aimed at identifying industries that would be compatible with Utah's environment and which might be attracted to the state. The new center is combined with the Engineering Experiment Station and will extend the station's traditional role of technical assistance to local industries to encompass environmental problems.

Congress: Much ado about water pollution amendments

Recent water pollution control laws must be wed with the Refuse Act of 1899



Senator Muskie



Senator Hart

The most pressing environmental matter before this 1971 legislative session of Congress is the messy business of amending and extending U.S. water pollution controls. Obviously, since the present legislation expires this June 30, the goal is to come up with a tough water law, like last session's tough air pollution control law.

One nagging problem in rewriting the law is clarification of some apparently overlapping jurisdictions and the legislative intent of environmental laws already on the books—the Refuse Act of 1899; the Federal Water Pollution Control Acts of 1965, 1966, and 1970; the National Environmental Policy Act of 1969; and the Fish and Wildlife Coordination Act.

The major effort will be to bring the Federal Water Pollution Control Act and its inherent concept of ambient water standards into harmony with the Refuse Act and its inherent concept of emissions standards. Nevertheless, it seems the Corps of Engineers will continue to enforce the Refuse Act and the Environmental Protection Agency's (EPA's) Water Quality Office will enforce the more recent water pollution laws.

Searching questions

After several rounds of hearings, the consensus maintains that the numerous suggestions already aired, for example, during last year's hearings (ES&T, November 1970, page 888)—effluent standards, streamlining of enforcement proceedings, increase in penalties, extension of federal law to all navigable waters, removal of distinction between intrastate and interstate water, and the like—should without much further argument be included in this year's amendments. Most probably they will be added. But more evident, as discussions continue, is the need for a complete reshaping of the legislation with a fresh, new, national rationale before the public loses its strong desire for the enhancement of the nation's waters.

While the Senate Subcommittee on Air and Water Pollution explored the status of the EPA program on water quality, joint Senate–House hearings of the Senate Commerce Subcommittee on Environment and the House Government Operations Subcommittee on Conservation and Natural Resources aired the basic 1899 Refuse Act. The joint hearing raised searching and fundamental questions not only on the necessity for the Corps' permit program, which was announced by Executive Order last December 23, but on its very legality.

Thus, while one quarter seeks clarification of recent water pollution control legislation, another quarter is resurrecting the 19th century law with its baroque legal language. So, the race is on to see which of the two can more quickly afford the nation the water quality that has been promised to it ever since passage of the 1965 act.

Water quality status

In its preliminary oversight hearings on water pollution, Sen. Muskie's air and water pollution subcommittee concentrated on five specific concerns—funding and manpower, regulations to be issued by the EPA, state certification required by the Water Quality Improvement Act (WQIA) of 1970, water quality standards, and effluent guidelines. On another day of hearings, the center of attention was clarification and interpretation of the 1970 act, specifically the status of vessel pollution, oil pollution, and again, the difficult question of state certification.

In his first official appearance before the subcommittee, the administration's star witness, EPA administrator William D. Ruckelshaus brought the Senators up to date on these items. On financing, Ruckelshaus said that no reimbursables—the monies advanced by states to meet the federal share of construction funds—have been paid to date. By the end of last year, the federal government owed the 22 states which prefinanced the funds a tidy sum of $1.5 billion. But, of the $800 million appropriation for fiscal 1970, $100 million will be available for payment of reimbursables, perhaps as early as mid-May.

The subcommittee chairman referred to the lack of payment as an administrative lag, but the star witness differed with this interpretation and pointed out that the existing allocation formula was not responsive to the needs of some of the heavily populated states, such as New York and Michigan. Ruckelshaus agreed, however, that the federal government needs not only to get the monies to

Congressman Reuss

Common concern. *Chairmen of three congressional subcommittees ponder the best way to proceed, on an emergency basis, with the nation's water quality enhancement program*

the states but, in addition, to find cost-effective ways to do so.

Nevertheless, the federal government anticipates reimbursement of fiscal '70 and '71 funds and will probably start payment to the states by the beginning of fiscal year 1972. Already, federal officials have met with Gov. Rockefeller and indicated that New York will be receiving from $100–200 million in reallocated funds.

On effluent discharges, acting commissioner of the Water Quality Office, David D. Dominick indicated to the subcommittee that the purpose of the office's waste water inventory (ES&T, January 1971, page 20) is to canvass 22 basic industries, thereby obtaining discharge data, so that the federal government would be able to define the term "industrial equivalent of secondary treatment."

On the manpower issue, the nation entered 1971 with a manpower shortage, including a backlog of 30,000 persons in the water pollution control field. The precise number and distribution are not available, but a study authorized by the 1970 WQIA presently is looking into the needs for all phases of the water program; a report is promised by mid-year.

The old issue of water quality standards seemingly is becoming more and more of a roadblock to progress and, in particular, with respect to the state certification requirement of section 21(b) of the Water Quality Improvement Act. For example, if a state has given its certification on a particular interstate water and the EPA disagrees, then EPA is the final arbiter on questions on violation of standards.

The problem that becomes difficult to resolve occurs when enforcement actions are considered. Slightly more than half of the states, actually 27, have had federal–state standards for interstate waters fully approved. On the other hand, 44 states have state standards for intrastate waters (no federal jurisdiction); five—Arkansas, Delaware, Kentucky, Tennessee, and Wyoming—do not have standards for intrastate waters, which are not covered under the existing 1965 law and its amendments.

Permit program

In a later round of joint House–Senate hearings, the 1899 Refuse Act, which was resurrected in 1969, was the center of discussion because of the new twist of its permit program by the Corps of Engineers. Some circles maintain that the permit program may be the long needed panacea for the nation's water quality ills; others question not only the need, but even the legality of the program. President Nixon's chief environmental adviser, Council on Environmental Quality's Chairman Russell Train, hailed the program as the single most important step this country has ever taken to abate water pollution. So, the race is on to see whether the old law or the recent laws of the past six years are best equipped to proceed, on an emergency basis, with the nation's war on water pollution. Many maintain that the Corps' program may be the nation's best line of defense against polluters.

Although the Corps' guidelines for the issuance of permits had not yet been officially announced at press time, Shiro Kashiwa, assistant attorney general of the Land and Natural Resources Division in the Justice Department, told the joint hearings that the Justice guidelines of June 13, 1970 were withdrawn. What this means to U.S. attorneys general throughout the country is they are once again authorized to initiate civil or criminal actions referred to them by Corps district engineers or EPA regional representatives (ES&T, January 1971, page 13). Kashiwa indicated that the Justice Department's new instructions are effective when the Corps' guidelines are issued.

Then, ways to strengthen the permit program were discussed; more than likely the following suggestions will be included when the program is officially announced:

- The permit application must be signed by a company executive;
- False statements in the permit application may be prosecuted under 18 USC 1001; violation incurs a penalty of five years imprisonment or a $10,000 fine;
- Citizens will be able to review the permit applications in the Corps' district offices;
- A boilerplate clause in the application, requiring effluent charge considerations.

Whether the new water pollution legislation contains more deadlines than last year's air pollution legislation is of little consequence. What is needed now is a combining of the two water laws—the Refuse Act and the Federal Water Pollution Control Act—and clarification of the judicial test to be used in enforcing the new law. Whether to require an effluent test or an ambient water standards test is a controversial issue that will require much more discussion and interpretations as the hearings continue.

Not until this issue is adequately resolved can the nation make progress in its long overdue program for water quality enhancement. If Congress does not resolve this basic issue in this year's amendments, it will truly return to haunt them at some later date.

What will emerge in the way of new controls for water enhancement this session is far from clear at this time. What Congress has thought it was doing in the last six years for enhancement of water quality is not necessarily what today's status would show. SSM

Lead smelting plant controls air emissions

General Battery Corp. sets the pace with an enviable precedent for industrial cleanup

Harry J. Noznesky—GBC's president. *"Most of the citizens' complaints were traced to the smelting operation, so this is where GBC concentrated first."*

As the world's leader of a certain product, if your company were faced with a court order to abate air pollution emissions resulting from the manufacture of that product, what would you do? Close shop, move production facilities to a remote area, or control emissions, knowing full well that controls are expensive. Such a question might be posed by any one of a growing number of air pollution games today. But in a real situation it has happened to the General Battery Corp., and they have decided to control emissions. Perhaps their precedent will set the pace for other industries to follow.

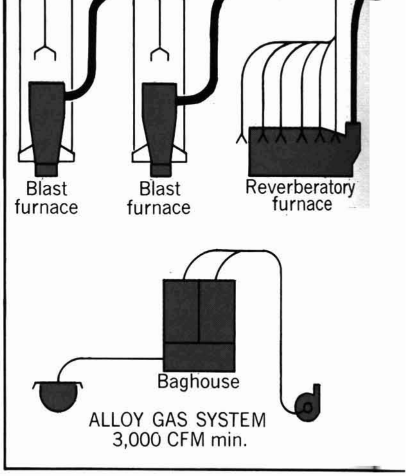
General Battery Corp. (GBC), a manufacturer of replacement batteries, this month opens its new secondary lead smelting plant in Reading, Pa. "The new plant represents a financial investment of approximately $3.5 million," says Harry J. Noznesky, president of GBC. "More than $1.5 million goes for air pollution controls at the new smelter."

GBC reclaims, or in today's solid waste jargon recycles, batteries. The company recovers lead from old batteries, resmelts the lead, and uses it to make new ones. Earlier, GBC had two smelting plants in its business operation, an old one at the Reading site which, incidentally, is located in a valley—and another in Hamburg, Pa. The Reading smelter started operation in 1933, nearly 40 years ago.

Both old plants were the sources of numerous public complaints and a court order from the Pennsylvania Department of Public Health. Each of the plants was capable of producing 6500 batteries per day. GBC batteries are produced for major oil companies, including Atlas, and auto accessory stores. The new Reading plant will have 28,000 ft^2 of floor space and is capable of accommodating the smelting operations of the two earlier plants. Rather than have two old plants within 15 miles of each other, GBC decided to build a new lead smelting plant with adequate air pollution controls for today, tomorrow, and the future.

Operations

Approximately 80% of the lead that is used in batteries is recycled, according to the Lead Industries Association (N. Y. City). As part of its customer service, GBC picks up old batteries from locations throughout the U.S. when it delivers its product, replacement batteries. In fact, trailer cargoes of old batteries are routinely delivered to the Reading smelter.



What GBC does in its recycle operation is to shear off the tops of old batteries, spill the contents from the battery case, and resmelt the lead for subsequent use in the manufacture of replacement batteries. The lead is then melted in either one of two blast furnaces in GBC's new plant or in its one reverberatory furnace. The three furnaces can produce as much as 100 tons of alloyed lead daily. Antimony content in the alloy is the critical controlling step.

What happens to other items in the operation? The battery cases are crushed and used as landfill. All equipment in the shearing operation must, of necessity, be acid-proof. All water and acid from this shearing operation are collected, retained, and subsequently neutralized to eliminate acid before discharge to a water course.

In 1963, all battery cases were made of rubber. But since then, the amount of plastics that is used in cases has increased. Today, many cases are all plastic; some are made of polystyrene, but others are made of high-shock polypropylene. The lead from the old batteries is contaminated with solid particles from the casing which adheres to the lead. So, when the lead is resmelted, odors resulting from the plastics are produced.

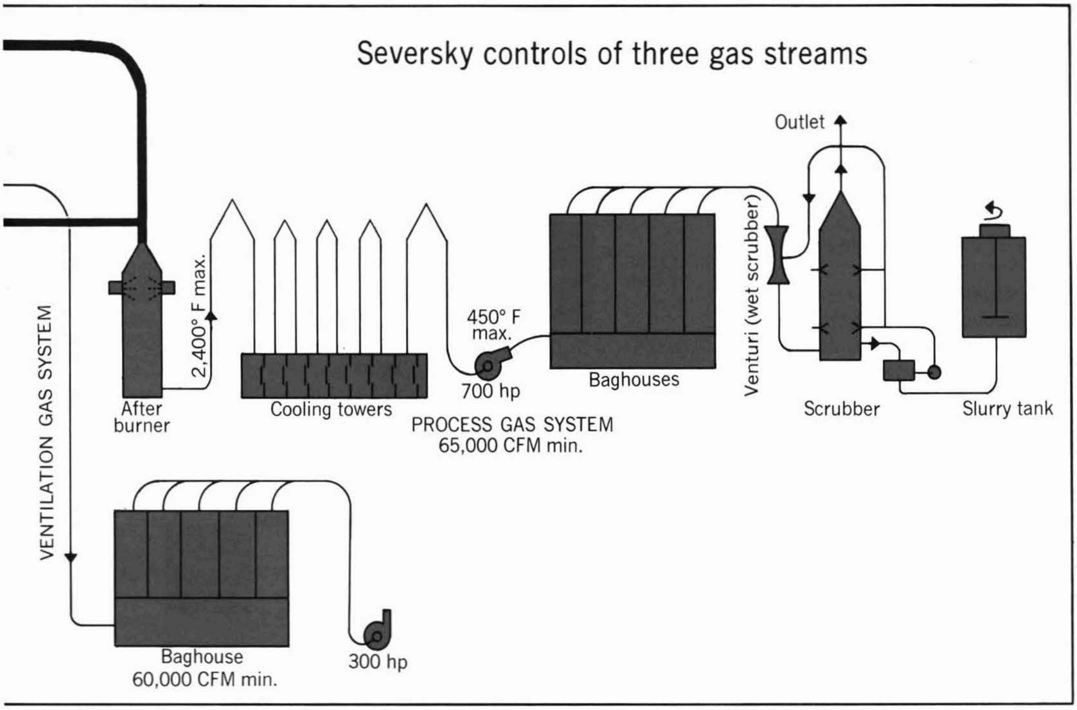
Pollution controls

Seversky Electronatom Corp. is the engineering firm that is under GBC contract to design, install, and make workable the air pollution control systems that will satisfy not only the public's complaints but also the requirements of the Pennsylvania Department of Public Health, which instigated the court order. Odors are one type of complaint, but other emissions include SO_x, lead oxide, and lead aerosols from the smelting operation.

The Seversky firm has the solution to the air pollution hazard from the smelting plant. Odors are disposed of by incineration at a high temperature (2400° F); lead oxide emissions and lead aerosols are trapped by baghouses. But, before the hot gases are passed through the baghouses, they must be cooled. So, 14 cooling towers are included in the design; they reduced the temperature of the gas from 2400° F to less than 450° F. Lead oxide emissions resulting from the ventilation and alloy systems also are removed by baghouses. SO_x emissions are scrubbed out with a venturi scrubber and mist eliminator.

In order to meet requirements for a cleaner environment, GBC's decision was to build a completely new smelter with the most advanced air pollution controls, to become a better neighbor in Muhlenburg Township, to provide employment for local residents, and to set the pace for oncoming air pollution controls.

To be sure, the Clean Air Amendments of 1970 started a new ball game for air pollution controls. GBC should place high in the industrial league for clean air. For the sport fans, Noznesky was a baseball pitcher of some renown earlier in his career, and GBC's chairman of the board, William Shea, is the man for whom the stadium in New York was named! SSM



Seversky controls of three gas streams

A specialized chemical conversion industry takes wastes from petroleum refineries and manufactures marketable products

Reclaiming industrial waste water

Today, recycle is *the* word in environmental circles, especially among businessmen who foresee reclamation as a profitable step in industry. While the treatment of gas, liquid, or solid wastes is more or less already required, recycling has yet to become a completely adopted practice.

Reclaiming waste streams from petroleum refineries is an example of potential pollutants becoming a successful chemical business. Merichem Co., based in Houston, Tex., represents one of the first such recycling ventures. "All of the materials that we bring in are totally recycled back into the economy," stresses A. Roy Price, executive assistant to Merichem's president. Many of a refinery's highly toxic waste streams contain valuable chemical compounds which can be recovered and marketed.

Waste caustic, produced in manufacturing gasoline, contains on the average 20–30% alkalinity (used to reduce the sulfur content of fuel). The caustic treating process, widely employed for many years, is still used in the newest refineries and is one of the most economical ways to sweeten gasoline. Besides removing sulfur compounds, caustics also extract organic acid materials. Although not true acids chemically, these organic materials, classified generically as phenolics, are commonly called cresylic acids.

The caustic solution, containing 20–30% dissolved organic materials after its reaction with gasoline, used to be dumped into the refinery effluent and discharged into the plant's receiving body of water. Pollution became a serious problem for two reasons: the alkalinity of the discharge was too high, and the phenolic materials (cresylic acids) are highly toxic, especially to fish and vegetation. Furthermore, drinking water supplies could become contaminated. Toxicity is not the problem here (dilution reduces toxicity); taste is. Phenolics have some of the lowest taste thresholds of any organic material. When a drinking water supply receives the usual chlorine treatment, phenolics become chlorinated. This chlorinated form has a low taste threshold of 2–5 ppb. Therefore, no phenolic material should be allowed in any surface water that will eventually be used for drinking.

Process

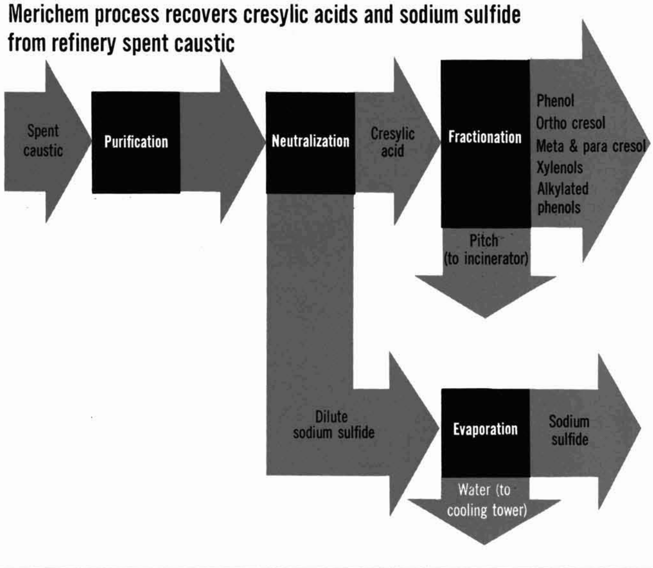
In the late forties, John Files, president of Merichem, developed a process that recovered cresylic acids from waste caustic solutions. This process was developed commercially before the present push on pollution control. Presently, 700 million pounds of waste material are processed and marketed annually.

Here's how Merichem recovers cresylic acids from refinery waste streams. The process begins (see flow sheet) with a purification step that separates the organic sulfur compounds and hydrocarbons from the cresylic-rich caustic mixture. The mixture is neutralized which causes the dissolved cresylic acids to separate out and float to the surface. This upper organic layer, further purified and separated by fractionation, is divided into phenol; *ortho-*, *meta-*, and *para*-cresol; xylenols; and alkylated phenols. All the components of this organic layer are marketed to industry, except for a heavy-bottom pitch.

The heavy pitch, collected during the cresylic recovery process, is burned in an incinerator. One common problem encountered in burning pitch is difficulty in sustaining combustion. The secret is atomization or breaking up the heavy residue into small droplets. Each particle is then surrounded by enough oxygen for complete combustion. If the residue is not atomized, incomplete combustion takes place with a resulting heavy black smoke.

The system Merichem adopted uses sonic energy—a high velocity steam jet that shears the pitch particles. The pitch, kept in a molten state at temperatures above 300° F, and process air are injected with the jet stream into the incinerator. The high velocity steam shears the molten pitch into finely divided droplets.

Merichem process recovers cresylic acids and sodium sulfide from refinery spent caustic



The bottom, aqueous layer (after neutralization) contains a dilute sodium sulfide solution (Na_2S or NaHS). This is concentrated and evaporated before being marketed and sold. Inorganic salt solutions form the second category in Merichem's product line, the first being organic compounds.

Pollution control

Besides being part of the pollution abatement program for some 100 different refineries, Merichem has developed two internal waste disposal systems (for air and water) for its recovery process. In purifying organic materials, large quantities of air are needed. Also, the organic compounds contain large amounts of sulfur picked up during gasoline purification steps. These organic sulfur compounds (the mercaptans) may be quite odoriferous.

Steps are taken to prevent air pollution from the recovery process. If an air stream is vented to the atmosphere, it must pass through a caustic scrubbing unit that removes soluble organic sulfur compounds. Since no unit is foolproof or can operate 100% of the time, a back-up system collects the waste gas streams after passage through the scrubbers and feeds them to an incinerator. Any remaining gases are burned odorlessly and vented to the atmosphere as sulfur dioxide (SO_2), carbon dioxide, and water. The SO_2 occurs in such small amounts that no air pollution is created.

The waste caustics from gasoline refineries contain about 20–30% sodium hydroxide and organic matter chemically combined with sodium hydroxide. In fact, the term for this material is sodium cresylate. The rest of the solution is water. Some of this water leaves the plant in the 30–40% sodium sulfide products. However, when the sodium cresylate enters the process separation step, the aqueous layer is very dilute—only 15% sodium sulfide. Large quantities of water are removed in the evaporator. This water, even though distilled, may still contain trace quantities of sulfides or phenolics and, consequently, cannot be discharged to the receiving body of water (in this case, the Houston Ship Channel).

Because of the water's low mineral content after distillation, it is used internally as cooling tower makeup water. The Merichem plant has no process water discharge into the Houston Ship Channel. The only effluent is a small amount of blowdown from the boilers, this is treated and discharged. Merichem has a state-issued permit to make the discharge.

The water control system also consists of dikes and drains. The entire plant process area is diked on concrete slabs with drain lines and sumps that collect all rainwater. To eliminate the risk of ground contamination from the runoff, this water is pumped into the process system. In this way, rainwater which would ordinarily wash the area and run off into the bayou will not pollute the receiving water.

Markets

Merichem produces 70 million pounds of cresylic acids annually for use as plasticizers for plastics, as synthetic lube oils, gasoline additives, or hydraulic fluid. Also, cresylics are sources of phenols, cresols, and xylenols.

The pulp and paper industry is the main consumer of sodium sulfide (a replacement for salt cake or sodium sulfate in the digestive proceses). A pulp mill, before using sodium sulfate, has to reduce it to sodium sulfide. Merichem's material, already in the form of aqueous sodium sulfide, can be used directly in the digesting system.

Full-scale commercial shipments of sodium sulfide are going directly into pollution abatement. Added to effluent streams, it will precipitate heavy metallic metals (lead, mercury, zinc) out of solution. For example, mercury, in the presence of a sulfide ion, forms a mercurous sulfide precipitate that is highly insoluble. (See "Mercury in the environment," ES&T, November 1970, page 890). This precipitate settles and can be removed from the effluent stream before it is discharged.

Economics

In the U.S., about half of the cresylics in gasoline is presently being recovered by caustic treating. Nevertheless, most of the other 50% is also recoverable. The technology is available for almost 100% recovery of the cresylics in gasoline, according to Merichem.

The entire concept of making money from wastes sounds ideal, but this is far from the full story. This industry, emphasizes Merichem's Price, "is in the chemical business, and the markets for our products go up and down with the fortunes and failures of the chemical industry." First of all, Merichem pays for the wastes it receives. It's a waste material to the refiner, but is purchased, transported, processed, and then marketed.

Freight is a large expense, even though Merichem has its own barge system. Hauling materials that are 80% water results in small payloads. Also, markets have to be developed—sodium sulfide has been used by the pulp and paper industry only for the past few years. Pollution control within the plant itself must be considered as an expensive (although, of course, necessary) item.

Lastly, the materials marketed often have to compete with synthetics. The cresylics compete with organic synthetic cresylics and coal tar-derived cresylics. The sulfide competes with salt cake and sulfide manufactured from other processes. In short, these products are in constant competition. Revenues realized are also subject to the cycles of the chemical industry.

Some chemical producers are saying that the supply of waste material for cresylic manufacture is drying up. However, Merichem does not foresee any drastic changes. Hydrogenation is sometimes used as a method for sulfur removal rather than the caustic treatment, but while it more thoroughly removes sulfur, hydrogenation is more expensive. On the whole, refineries are not using this instead of caustic treatment; in fact, some refineries use both processes. An added incentive is the revenue benefit from selling caustic solutions to such plants as Merichem. Says Price, "You'll find some refineries abandoning caustic treatment in favor of hydrogenation, but this is not an overall trend. For every one that does, there is another going the other way."

New ventures

With its already developed collection and transportation system established east of the Rocky Mountains, Merichem stands ready to apply its waste-to-marketable-product concept to other industrial wastes. In fact, the company is mounting a major diversification program toward recovering additional salable materials. "We're a specialized chemical conversion system," explains Price; "besides being in the chemical business, we are in the pollution abatement industry in the sense of recovering economic material from industrial wastes." CEK

Master plan for Hilton Head Island

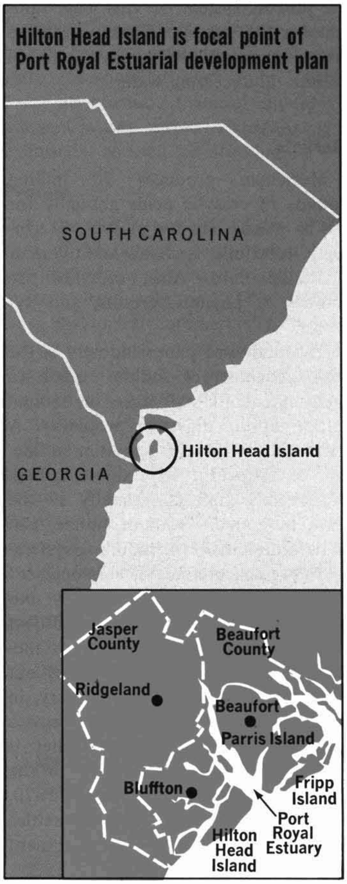
Privately commissioned study details ecologically oriented development plan for Port Royal estuarial region

Islands are hard to come by these days. Especially the ones with large chunks of undeveloped, inhabitable land. At least one such island still exists, however, and its major landholder wants to make certain that the unique way of life offered by island living isn't spoiled forever by piecemeal development and careless land use.

The property in question is Hilton Head Island—a semitropical, sun-soaked spot in the center of the Port Royal Sound estuary off the coast of South Carolina. In June of 1969, the Hilton Head Co., which owns virtually all the remaining developable land on the island, commissioned Skidmore, Owings & Merrill, a Washington-based architectural and planning firm, to develop a long-range land use program to ensure orderly development of its holdings without sacrificing the ecological integrity of one of the nation's few remaining unspoiled estuaries. The study, financed entirely by the Hilton Head Co., is the first of it's kind ever undertaken by a private firm.

"The uniqueness of the project cannot be understated," says John W. Galston, associate partner and leader of SOM's study task force. "How often will you find an 11,000-acre holding on a coastline in the control of one group of individuals?"

Hilton Head Island, according to Galston, is an "ecological paradise." The largest of the sea islands on the south Atlantic coast (28,000 acres excluding tidal marshes), Hilton Head houses one of the most extensive rookeries in North America. Some 285 species of birds inhabit the island as well as the various forms of marine life which spawn in the sizable tidal marshes. And while alligators may not have the immediate appeal of egrets, Galston notes that Hilton Head marks the northern-most native habitat of these vanishing reptiles.


Hilton Head Island is focal point of Port Royal Estuarial development plan

For all its natural beauty, however, the Port Royal Sound estuarial region—including Hilton Head, several smaller islands, and adjoining Jasper and Beaufort counties—suffers from unemployment and an inadequate tax base. Although it represents only 7% of the land area of Beaufort County and houses only 7% of its population, Hilton Head Island foots one-quarter of the county's tax bill.

Industry sought

In an effort to beef up the regional economy, then South Carolina's Governor Robert McNair wooed West Germany's U.S. subsidiary of Badische Analin und Soda Fabrik (BASF) and offered, among other things, a five-year exemption in ad valorem taxes if the chemical giant would build a $200 million dyestuff and styrene complex in Beaufort County. The plant was to be built on an 1800-acre site located on the Colleton River at Victoria Bluff and would have imported 40,000 barrels of naphtha per day as feedstock. Advocates of the plant argued that BASF would have provided employment for about 600 people and would double the tax base, thereby stabilizing the economy of the region.

The BASF proposal raised the hackles of members of the local fishing cooperative, the Citizens' Association of Beaufort County, and Hilton Head developers, among others. Even if the plant provided the promised number of jobs—a contention which Hilton Head developers rejected—they charged that the 2.5 million gal. of effluent per day which would pour into the Colleton River would destroy oyster, crab, and shrimp fishing in the area. Leakage from oil tankers during the unloading operation would foul the water, they claimed, and there was no protection against accidental spills.

A spate of lawsuits and delaying maneuvers by various environmental action groups resulted in an announcement by BASF in January of this year that it had abandoned plans to build at Victoria Bluff.

During the scuffle with BASF, Skidmore, Owings & Merrill suspended their development study. "We knew we had to fall back and regroup," Galston said. Hilton Head Co. was advised to delay further work on the master plan for land use on the island, and SOM agreed to "be available" to discuss environmental issues.

After the capitulation of BASF, Skidmore, Owings & Merrill resumed work on the master plan and a time-phase development program, which set 5, 10, and 20-year goals for the island. Basic to the development of Hilton Head, says Galston, is the realization that the island is not an isolated patch of ground, but an integral part of an economically depressed, two-county area. Accordingly, the SOM study attempts to identify major influences on regional development and assign priorities to the needs of area inhabitants.

"There are certain natural characteristics about growth and development which have been almost entirely neglected by the people in the two counties," according to Galston. The area is rich in natural resources which have scarcely been tapped, he says, and the introduction of heavy industry would have been "an artificial stimulant which ultimately would have destroyed more than it would have produced."

Fishing and shellfishing efforts should be intensified, he believes, and cooperative farming would give a tremendous boost to the economy. Aquiculture—catfish and shrimp farming—should also be explored for their economic benefit, according to Galston.

Heavy industry, the SOM report concludes, belongs in Savannah, Ga., where it is already located. Other "compatible" industry, however, should be encouraged in the two-county region. Spinoff industries, such as canning or freezing of vegetables and shellfish could augment the economic stability of the region. "The concept of farming is understood by the community," Galston points out, while petrochemicals represent a "complex and highly technical process which bears no relation to the area whatsoever."

In addition, a growing opportunity exists in the prefabricated or modular housing industry, according to Galston. The two-county area, he points out, has large stands of southern yellow pine which remain to be exploited. Such light industry should complement the seasonal fishing and farming operations and provide steady, year-round employment for many semi-skilled and skilled workers.

The SOM report details several basic criteria to be met by new industry. A desirable industry should not require large amounts of capital to get it off the ground and should be able to start up without a large construction lag time. There should be a market already in existence for the product or service, and raw materials should be readily available. New industry should rely chiefly on local labor, the report says.

In addition to the income realized from light industry, Hilton Head Island itself could bolster the economy by serving as a focal point for increased tourism, according to the SOM report. New jobs in hotel management and tourist services could strengthen the now weak tax base. The Hilton Head Co. is urged to plan low and moderate income housing on the island as well as luxury vacation homes, hotels, and retirement properties. Construction should be by local firms and patronage of local businesses is to be encouraged.

Transportation

A successful mass-transit system is seen as the key to realizing the potential of the estuarial region. SOM has recommended a water shuttle-bus system which would connect both Hilton Head and Fripp islands with Savannah, Ga., Beaufort, and Bluffton, S. C. Besides the economic benefits to be derived from a locally owned and operated mass-transit system, the water-bus would hopefully curtail the number of automobiles used on Hilton Head. Automobiles on the island might then be restricted to residents, with tourists depending upon public transportation. The technology for such a water-bus is available, says Galston, and it would be possible to use existing waterways without additional dredging.

Spanish moss. *Regional development plan would upgrade the economy, but not at the expense of natural beauty*

The SOM study also gives considerable attention to preserving the environment on the island while developing recreational facilities. "The amount of leisure time that people have is nearly as great as the amount of time that they work," Galston says. "The market for this kind of development has never been greater, yet at the same time the potential destruction that poor land utilization and planning can bring to an area is equally frightening."

Galston sees the Hilton Head study as a prototype with implications ranging far beyond the confines of the Port Royal Sound estuary. A greater sophistication in the way people think, he feels, will bring more and more pressure for national land use policies. "People are going to get a lot more sensitive as the figures on land use come home to them," Galston says, "and they will demand policies of land use that reflect conservation. The greatest asset Hilton Head has is 11,000 acres of land to which nothing has been done. You can clean up polluted air and water, but once you destroy land, the cost of restoring it is phenomenal."

Although he concedes that the political climate in South Carolina is less than totally favorable to the type of program SOM proposes, Galston points out that the state has a new administration and that the current governor has not committed himself irrevocably to a course of action as did his predecessor. Hilton Head President Fred C. Hack concurs. "Rumblings continue to be heard in state government quarters," Hack says, "but we feel this is only from a few diehards who prey on the uninformed to support their self-acquired privilege to exploit our inherited environment."

Galston and SOM approach the future with cautious optimism: "Before, they all thought the great industrial complex was the Holy Grail," he says. "Now at least the door is open." HMM

Pyrolysis of refuse gains ground

Enviro-Chem goes commercial with Landgard system, BuMines converts city garbage to fuel

In major urban areas, the headaches—like the garbage piles—just get bigger and bigger. The old methods of solid waste disposal—bailing, bagging, barging, burying, and burning—become increasingly less attractive as space runs out, construction and handling costs soar, and pollution control standards become more rigid.

But some relief may be in the offing with a brand new, old process—pyrolysis. The old part is technology. Scientists at the Bureau of Mines' Pittsburgh Energy Research Center have been studying pyrolysis in one form or another for years. The new part is a commercial package. Monsanto's Enviro-Chem Systems, Inc. has developed and field tested a 35-ton/day pilot pyrolysis plant—the Landgard system—and is ready to guarantee that systems capable of pyrolyzing up to 1500 tons/day of municipal refuse will meet all existing pollution control standards at the time the contract is signed.

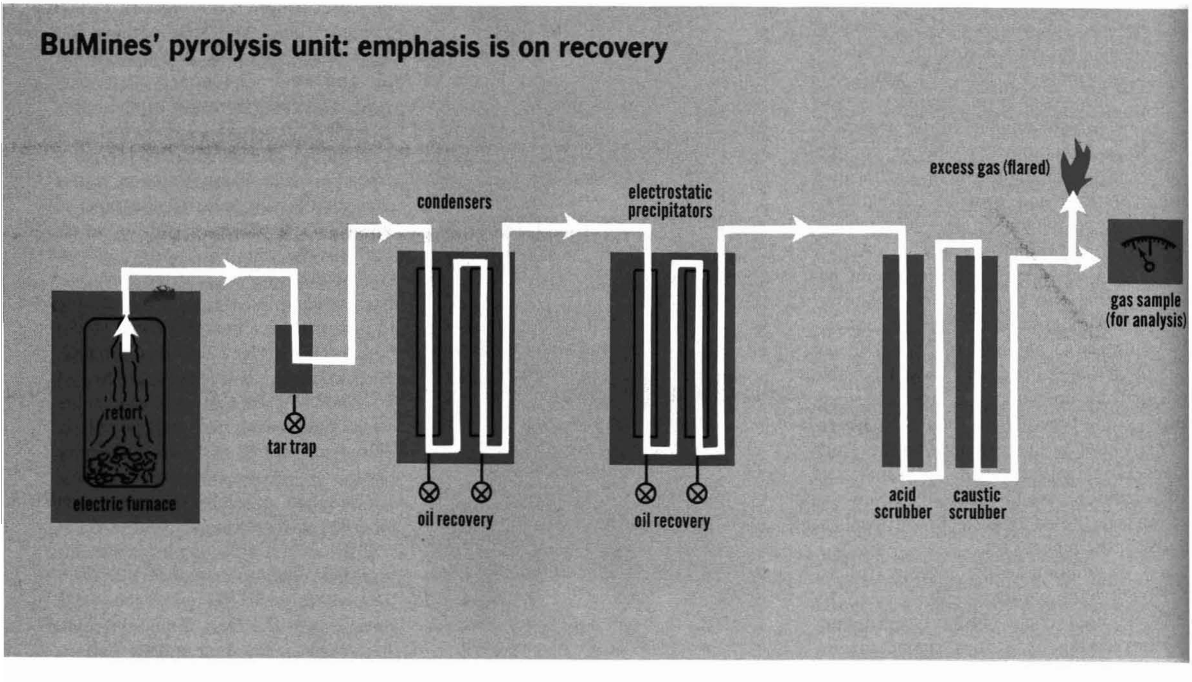
Pyrolysis (destructive distillation, carbonization) is simply thermal decomposition in the absence of air. Though the process is basically the same in both the BuMines and Enviro-Chem systems, the goals are slightly divergent. For BuMines, pyrolysis is a method of transforming trash into clean, usable fuels. For Enviro-Chem, pyrolysis represents a pollution-free, competitively priced method for getting rid of the mountains of garbage inundating major cities.

Work on pyrolysis at BuMines started nearly half a century ago with basic studies on the carbonization of coal. BuMines' pyrolysis unit, built in 1929, was designed to be a research tool, and features a complete recovery train for trapping pyrolysis products for analysis. With only minor alterations, the unit remains in operation today.

Among the first waste material to be studied at BuMines was rubber. Shredded tires from the Firestone Tire and Rubber Co. were processed in the unit. The products recovered were gas with a high Btu content, oil, and a solid residue with a high heating value, Each of the products could be burned cleanly, according to Martin D. Schlesinger, project coordinator for process technology. From a ton of tires with smoky heating value of 32.5 million Btu, about 95% of the heat could be recovered as products.

The BuMines team explored a vari-

BuMines' pyrolysis unit: emphasis is on recovery



ety of waste products, including plastic battery cases and shoe soles. Municipal refuse seemed a likely next choice. "After all," Schlesinger says, "refuse is simply 'young coal.' "

For pilot studies, BuMines collected samples of municipal trash from Altoona, Pa. Altoona was chosen because glass and cans must be separated from garbage by citizens in compliance with a local ordinance. Furthermore, the refuse is taken to a local mulch plant which shreds the trash so it is easy to obtain reasonably representative samples.

Pyrolysis of the refuse yielded a solid residue, gas and oil fractions, each with significant thermal value. Water in the feedstock and any water produced in pyrolysis were recovered as an aqueous fraction containing pyroligneous products—aldehydes, alcohols, acids, ketones, etc. Product distribution was dependent upon water content of the refuse and pyrolysis temperature.

Although the heating value of garbage is less than that of tires—about 10 million Btu/ton—the 160 million tons of municipal refuse generated annually in the United States still has significant potential for energy recovery, according to Schlesinger. Since it takes 1–2 million Btu in electrical energy to pyrolyze a ton of refuse, the net energy yield will fall between 6 and 8 million Btu/ton of municipal refuse or some 9–13 billion Btu/year nationwide.

The BuMines unit consists of a furnace heated with nickel-chromium resistors and a recovery train to trap products. Shredded refuse is sealed inside a retort to charge the furnace and heated to the desired temperature. Gases given off first pass through an air-cooled trap where tars and heavy oils condense out. Uncondensed vapors pass through a series of water-cooled columns where additional oils and aqueous liquors are removed. The gas stream passes through electrostatic precipitators to remove oil mist and from there to acid and caustic scrubbers. The scrubbed gases are passed through meters which direct 99% of the gas to flaring and 1% to analytical instruments.

Depending on the reaction conditions, one ton of municipal refuse yields 154–230 lb char residue, 0.5–5 gal. tar and pitch, 1.2–2 gal. light oil, and 11,000–17,000 cu. ft of gas, in addition to 80–133 gal. aqueous liquor, and 18–25 lb ammonium sulfate. Typical thermal values for the products are: char, 8–13,000 Btu/lb; oil, 150,000 Btu/gal.; and gas, 500 Btu/cu ft.

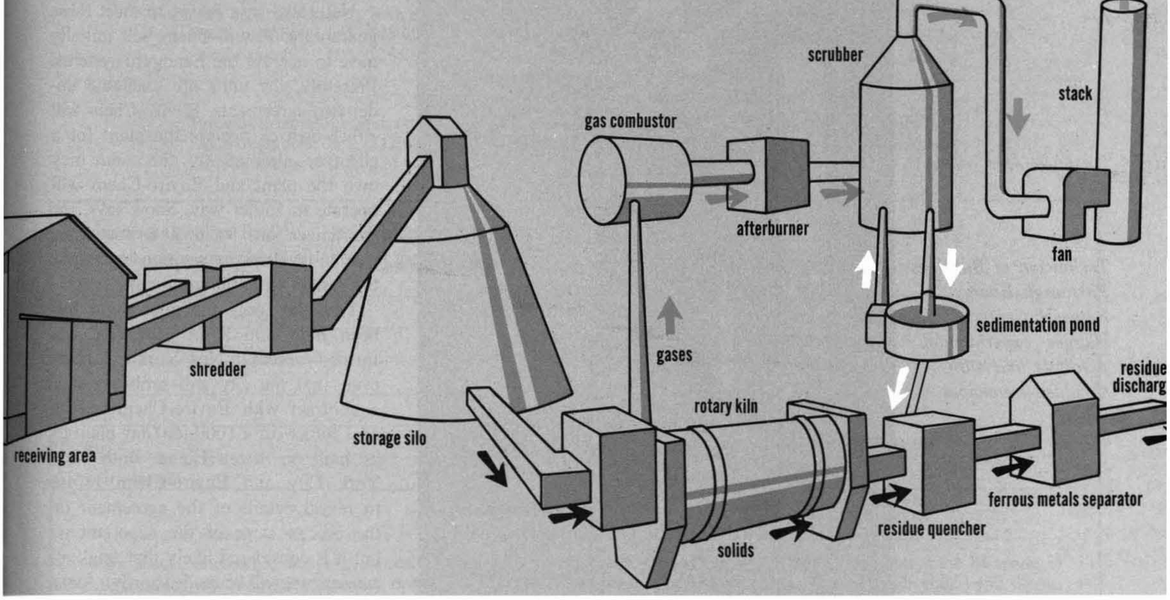
The economics of the plant operation depend heavily upon recovery of fuels. Although the BuMines operation is batchfired, it is estimated that continuously fed commercial plants taking advantage of revenue derived from fuel sales could bring the cost of waste disposal down to highly competitive levels. For a 500-ton/day plant, for example, BuMines estimates that disposal costs would be about $6.00/ton. For a 1500-ton/day plant, costs would be about $3.00/ton and for a 2500-ton/day municipal pyrolysis unit, costs might drop below $2.00/ton. BuMines is currently awaiting funds to begin construction and testing of a continuous feed pilot plant.

Enviro-Chem's Landgard

While the emphasis at BuMines is on maximum recovery of energy, Enviro-Chem takes a somewhat more practical view. It's not that Enviro-Chem has anything against recovery, according to Curtis M. Snow, manager of Commercial Development for Solid Pollution Control, but simply that the company wants to tackle the most pressing problem first—disposing of solid waste. Indeed, the Landgard system is sufficiently flexible to allow recovery of resources, Snow says, but he adds, "what good does it do to recover goodies from solid waste if you can't find a home for them in the economy?"

The Landgard system is designed to be a totally enclosed, self-contained operation. Refuse is trucked to an enclosed receiving area (kept under slight negative pressure to control

Enviro-Chem's Landgard: first get rid of the waste



dust and odors) where it is dumped into a pit. Enclosed conveyors carry refuse to shredders where rubbish is reduced to a fairly homogeneous mixture with particle size about 3–4 in. in diameter. A second conveyor system removes refuse from the shredder and dumps it into a storage silo.

From the silo, refuse is conveyed to a rotary kiln. The kiln is lined with refractory material and there are no grates or moving parts to clog with metal or plastic. The kiln is slightly inclined from exit to entrance so charred material falls by gravity into the water quenching unit. The residue is water-cooled before passing to a magnetic separator which removes ferrous metals. The wet residue—reduced from the original trash volume by 94%—is then loaded into trucks and taken to landfill. Cooling water is diverted to sedimentation basins for recirculation.

Gases driven off from the kiln during pyrolysis are passed through a combustion chamber where hydrocarbons are oxidized. Complete combustion is assured by an afterburner module. Product gases—carbon dioxide, nitrogen, etc.—are passed through an adiabatic spray-scrubber and then released to the atmosphere. Steam plumes, which might be objectionable from a public relations standpoint, are eliminated by heating the stack gases. Since the gases are clean, Snow points out, very low stacks can be used except where otherwise required by local ordinance.

Enviro-Chem is proud of the flexibility of the Landgard system. Acid or caustic scrubbing can be added, Snow says, if the composition of waste makes it necessary to remove hydrogen chloride or sulfur dioxide. Metals separation may be done before or after pyrolysis, depending upon the market possibilities in the area.

Snow also points out that the system accepts municipal refuse as it is. No hand separation procedures are necessary, he says.

Enviro-Chem claims capital and operating costs are roughly two thirds of the amount necessary for pollution-free incinerators. Total operating costs to a city for an Enviro-Chem operated plant would be about $7.50–8.50/ton. Further, resource recovery and recycling (R&R) could figure in the economics of Landgard. Scrap iron and aluminum are the most ready markets. Carbon from the residue could be used in sewage treatment plants and excess heat could be trapped and used to generate steam.

But R&R still has a lot of developing to do before it becomes practical, Snow asserts. "Recycling and recovery holds a lot of fascination for politicians and the lay mind," Snow says. "There's been a lot of garbage generated about garbage." The technology for R&R is not a major handicap, Snow says. Rather, the most difficult challenge R&R faces is finding a place in the economy where recycled resources can be used. There is, he points out, a cyclical pattern by which contamination builds up as material is recycled and recycled again. Recycling uses, he maintains, must be carefully selected to ensure necessary quality and to fit in the economic picture. "There are lots of wonderful things you can do with science," Snow remarks, "but you can't always afford to do them."

Guarantees

Even if its pyrolysis unit isn't the last word in R&R, Enviro-Chem figures it has at least one other strong selling point. That is its system of guarantees. It guarantees throughput capacity, maximum operating costs, and putrescible content of the residue. In addition, the company agrees to meet all existing air and water pollution standards in effect when the contract for construction is signed. The company guarantees the specs of Landgard or it will remove the unit and restore the land to its original condition.

Naturally, says Snow, to meet these guarantees, Enviro-Chem will initially have to operate the Landgard systems. Presently, the units are available under two agreements. Enviro-Chem will either own or operate the plant for a client or, alternatively, the client may own the plant and Enviro-Chem will operate it. Either way, Snow says, the guarantees are valid and customers will be in a unique position to try out the system with minimum risk.

Thus far, only the pilot plant has been built and is in operation. Informed sources in New York say, however, that the city will probably sign a contract with Enviro-Chem in the near future for a 1000-ton/day plant to be built on Staten Island. Both New York City and Enviro-Chem refuse to reveal details of the agreement or the precise stage of the negotiations, but it is considered likely that final arrangements will be made shortly. HMM

Technician at BuMines' Pittsburgh Energy Research Center charges experimental pyrolysis unit with shredded municipal refuse

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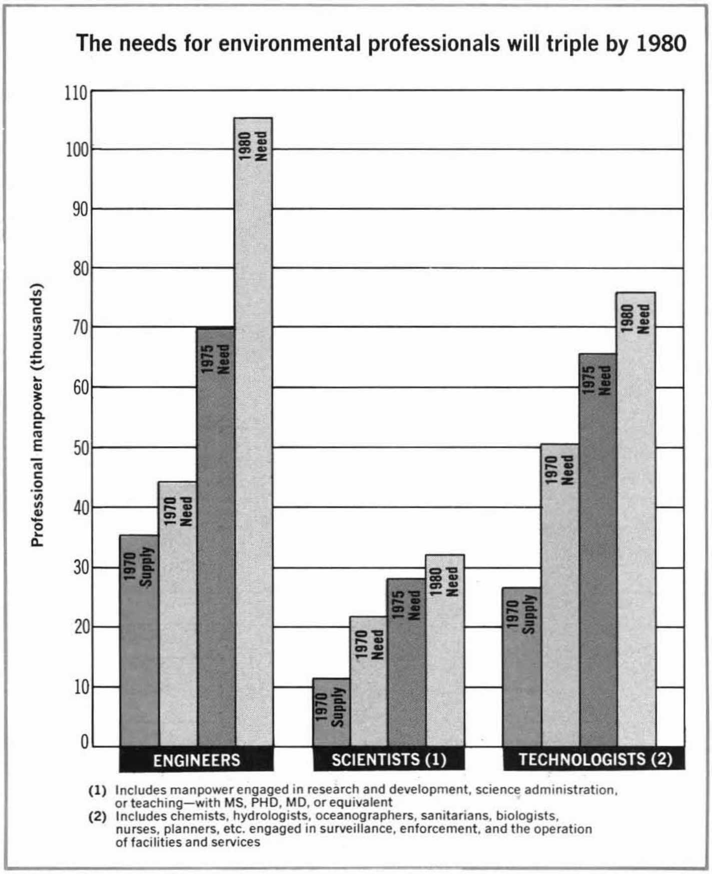
Manpower for environmental protection

By 1975, the need for trained, educated personnel engaged in environmental control will be double the present supply


The needs for environmental professionals will triple by 1980

(1) Includes manpower engaged in research and development, science administration, or teaching—with MS, PHD, MD, or equivalent
(2) Includes chemists, hydrologists, oceanographers, sanitarians, biologists, nurses, planners, etc. engaged in surveillance, enforcement, and the operation of facilities and services

Figure 1

Mushrooming public concern over environmental quality has resulted in a marked interest in the manpower needed to plan and implement prevention and control activities. Although this public attention is new, the basic mechanisms and technology have been developing for many years. Begun largely by the effort of health officers and sanitary engineers in providing safe supplies of drinking water, milk, and foods, the fields of action and the variety of professionals and technicians involved have expanded and extended into a broad-scale view of protecting or restoring the quality of modern environment.

Environmental protection represents a diverse area of work; thus, it draws heavily on a wide variety of professionals including chemists, physicists, and biologists of many specialities; hydrologists, meteorologists, and oceanographers; engineers, sanitarians, ecologists, physicians of several specialties; attorneys, mathematicians, statisticians; political scientists; planners, economists; and social scientists. They are engaged in • carrying out technical and administrative or legal functions concerned with *prevention and control programs,* • conceiving, designing, and constructing *environmental protection facilities,* • planning, implementing, and directing general and specific *service programs* (in-

Ralph C. Graber
Frederick K. Erickson
William B. Parsons

Environmental Protection Agency
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cluding public water supply and waste treatment equipment and facilities), • conducting relevant *research and development,* • *conducting investigations, surveys, and surveillance* programs, and • *teaching* at all educational and training levels.

There has been relatively little effort to assess the manpower situation in depth and over time. Deterrents to the development of such information are a lack of understanding or definition of the various professional and paraprofessional occupational roles and functions, and the need for occupational interpretation in terms of disciplinary versus categorical program specialization. Much effort is necessary to identify and measure factors of supply, demand, utilization, and production of environmental manpower.

In 1970, the total personnel employed in environmental protection exceeded 243,000 (Table I)—an estimate based on over 35,000 engineers, 37,000 scientists, sanitarians, etc.; 69,000 technicians; and 101,000 aides. The manpower needed to make significant improvement in environmental quality in 1970, 1975, and 1980 is estimated in Figures 1 and 2. The rate of increased demand for such manpower will be determined largely by the regulatory and fiscal impacts of federal, state, and local governments. Historically, environmental manpower assessment has been limited to two professions—engineer and sanitarian.

Engineer

Many **engineers** devote a major portion of their time applying engineering and scientific principles and practices to the prevention, control, and management of factors that may influence man's environment. During the last decade the need for a more comprehensive view of all environmental factors and their interrelationships has broadened the opportunities for engineers. Prior to that time, the engineer was concerned primarily with such factors as water supply and water pollution; therefore, the use of occupational title "sanitary engineer" was not inappropriate. The more comprehensive outlook validates the title of "environmental engineer."

Of the estimated 35,000 engineers employed in environmental protection activities in 1970, some 12,000 were the expanded counterparts of the earlier "sanitary engineers." The remaining engineers were engaged in some aspect of environmental protection in public works, in municipal services, or in increasing industrial attention toward preventing or controlling air, water, and land pollution.

Estimated 1970 levels of employment in which all or a major proportion of the engineer's activities was directed to environmental engineering number 35,800. Many engineers function in more than one environmental area; therefore, it is difficult to estimate the number employed in any one field, particularly relating to public water supply and water pollution, and even solid wastes. The classification of engineers employed by consulting firms which practice across-the-board is illustrative of this fact. For example, many of the more than 5400 professionals reported by those consultants listed in the "1970 Annual Yearbook of the Water Pollution Control Federation" also work on water supply and (or) solid waste management projects during any given year. However, the 1970

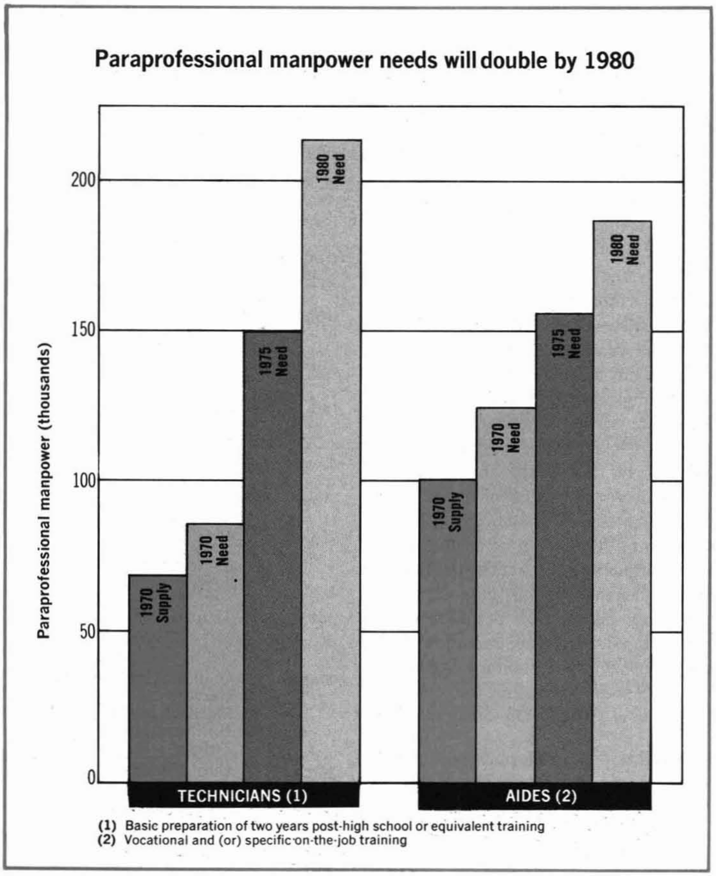

Figure 2

engineering billings on new facility plans of $6.9 billion for waterworks and pollution control, reported by *Engineering News Record* **186** (1), indicated a heavy weighting toward sewerage and water pollution control works.

With heightening concern over air pollution, water pollution, solid wastes, shortcomings in public water supplies, controllable hazards of the occupational environment, and the quality of environment in urban neighborhoods, the total requirements for engineers in planning, constructing, operating facilities, and monitoring the performance and environmental impact of such facilities can be expected to increase severalfold. Present need far exceeds present utilization, but the realities of probable public and private response to the need could well represent doubling engineering employment for environment by 1975.

A 1962 national survey showed that about one-third of the respondent engineers were employed by state and local governments, one-third by private industry and business, and the balance by the federal government or other organizations. Management or administration was the most important function and involved nearly one-third of the respondents.

Numerous professional organizations are concerned with the environmental engineering field. Eight have joined in sponsoring the Environmental Engineering Intersociety Board, Inc. (formerly the American Sanitary Engineering Intersociety Board, Inc.). The objectives of the board are to improve the practice, elevate the standards, and advance the cause of environmental engineering. Certification as a Diplomate of the American Academy of Environmental Engineers (AAEE) is awarded by the board, based upon compliance with educational and experience standards, state licensure, and satisfactory completion of written and oral examinations. Currently, the board certifies environmental engineers in four subspecialties—air pollution control, industrial hygiene, radiation and hazard control, and sanitary engineering. The AAEE roster at the end of 1970 lists over 1150 Diplomates.

Sanitarian

The **sanitarian** applies his knowledge of the physical, biological, and social sciences for the improvement, control, and management of the environmental factors which might af-

Table I. Environmental manpower needs now outstrip the supply

	SUPPLY	NEED		
Occupation	1970	1970	1975	1980
Engineer	35,700	44,000	70,000	105,000
Scientist	11,300	22,000	28,000	32,000
Technologist	26,600	51,000	66,000	76,000
Technician	69,500	86,000	150,000	214,000
Aide	101,000	126,000	157,000	188,000

Table II. Academic institutions offering environmental protection graduate (supported by selected federal grants programs)

		ENVIRONMENTAL AREA OF PROGRAM EMPHASIS[a]					
Location	School	Air	Ind. hyg.	Rad. protect.	Solid wastes	Water	Other[b]
Ala.	Tuskegee Inst.					X	
	U. of Alabama					X	
Alaska	U. of Alaska						X
Ariz.	U. of Arizona					X	
Ark.	U. of Arkansas			X		X	
Calif.	**California Inst. of Tech.**						X
	San Jose State					X	
	Stanford U.					X	
	U. of California, Berkeley		X			X	X
	U. of California, Davis					X	X
	U. of California, Irvine						X
	U. of California, Los Angeles			X			X
	U. of California, Riverside	X					X
	U. of Southern California	X					
Colo.	Colorado State U.			X		X	
	U. of Colorado					X	
Conn.	U. of Connecticut					X	X
	Yale	X		X			X
D. C.	Georgetown						X
	Howard					X	
Fla.	U. of Florida	X		X	X	X	X
	U. of Miami			X			X
Ga.	U. of Georgia						X
	Georgia Inst. of Tech.	X		X	X	X	X
	Emory						X
Hawaii	**U. of Hawaii**				X	X	X
Ill.	**U. of Illinois**	X			X	X	
	Illinois Inst. of Tech.					X	
	Southern Illinois U.					X	
	Northwestern U.			X		X	X
Ind.	**Purdue**	X		X		X	X
	U. of Indiana						X
	Notre Dame					X	X
Iowa	**Iowa State**			X		X	
	U. of Iowa					X	
Kan.	Kansas State U.		X				X
	U. of Kansas			X	X	X	
Ky.	U. of Kentucky	X				X	
La.	Louisiana State U.	X				X	
	Louisiana Polytech. Inst.					X	
	Tulane	X					X
Me.	U. of Maine					X	
Md.	U. of Maryland	X					
	Johns Hopkins	X		X		X	X
Mass.	**U. of Massachusetts**	X				X	X
	Harvard	X	X	X		X	X
	Massachusetts Inst. of Tech.						X
	Northeastern U.					X	X
	Tufts					X	X
Mich.	**U. of Michigan**	X	X	X	X	X	X
	Michigan State U.					X	X
	Wayne State U.					X	X
Minn.	**U. of Minnesota**	X		X		X	X
Miss.	**Mississippi State U.**					X	
Mo.	**U. of Missouri**					X	X
	Washington U.						X

fect man's health. According to the most recent figures available, an estimated 12,000 sanitarians were employed in 1968. Prior estimates by the Public Health Service combined the data for sanitarians and sanitarian technicians and showed about 5000 in 1950 and 11,000 in 1960 for the combined groups.

The first national survey of persons who regarded themselves as sanitarians was conducted in 1962. State and county governments were the major employers. Inspection, testing, and control were the major activities of half of those answering the survey questionnaire. Two-thirds indicated a specialization in milk, food, and meat technology.

Thirty-five states require the registration or licensing of sanitarians. In 1960, a model registration act was developed by the Sanitarians Joint Council which consists of representatives from the International Association of Milk, Food, and Environmental Sanitarians (3000 members), the National Environmental Health Association (6000 members), and the American Public Health Association. The minimum requirements for sanitarians under the model act are: • a bachelor's degree with a minimum of 30 semester hours of academic work in environmental health or in the physical and biological sciences, • at least two-years full-time employment as a sanitarian, and • successful completion of an examination given by a state registration board.

programs in 1970

Location	School	ENVIRONMENTAL AREA OF PROGRAM EMPHASIS[a]					
		Air	Ind. hyg.	Rad. protect.	Solid wastes	Water	Other[b]
Mont.	Montana State U.					X	
Neb.	U. of Nebraska					X	
N. J.	Rutgers	X		X		X	X
N. M.	New Mexico State U.					X	X
N. Y.	**Columbia**			**X**			**X**
	Cornell					**X**	**X**
	Adelphi					**X**	
	Manhattan College					**X**	
	New York U.	**X**	**X**	**X**		**X**	**X**
	Rensselaer Polytech.			**X**	**X**		
	Union College and Univ.						**X**
N. C.	North Carolina State U.	X				X	X
	U. of North Carolina	X	X	X		X	X
	Duke						X
N. D.	North Dakota State U.			X			X
Ohio	Ohio State U.		X			X	X
	U. of Cincinnati	X	X	X		X	X
	U. of Toledo					X	
Okla.	**Oklahoma State U.**					**X**	
	U. of Oklahoma		**X**	**X**	**X**	**X**	**X**
Ore.	**Oregon State U.**	**X**		**X**		**X**	**X**
Pa.	**Pennsylvania State U.**	**X**				**X**	**X**
	U. of Pennsylvania			**X**			
	Drexel Inst. of Tech.	**X**			**X**	**X**	**X**
	Temple	**X**		**X**			
	Thomas Jefferson U.						**X**
	U. of Pittsburgh	**X**	**X**	**X**		**X**	**X**
P. R.	U. of Puerto Rico			X			X
R. I.	U. of Rhode Island					X	X
S. C.	Clemson U.					X	X
S. D.	South Dakota State U.					X	X
	U. of South Dakota						X
Tenn.	U. of Tennessee			X			
	Vanderbilt	X				X	X
Tex.	**U. of Texas**	**X**		**X**	**X**	**X**	**X**
	Texas A & M U.			**X**			
	U. of Houston				**X**		
	Rice					**X**	**X**
	North Texas State U.					**X**	
Utah	**Utah State U.**					**X**	
	U. of Utah	**X**				**X**	
Va.	Virginia Polytech.					X	X
Wash.	U. of Washington	X		X	X	X	X
	Washington State U.	X				X	
W. Va.	West Virginia U.	X			X	X	X
Wis.	U. of Wisconsin	X				X	
	Marquette					X	
	Total, 103 schools	***33***	***10***	***32***	***13***	***73***	***63***

[a] Includes research training in each program.
[b] Includes one oı more of following, as illustrations: injury control, toxicology, systems planning, environmental biology, etc.

Three professional environmental health organizations have sponsored the establishment of the American Intersociety Academy for Certification of Sanitarians (AIACS). The academy is dedicated to recognizing the professional quality and achievement of the sanitarians in the various environmental health fields. Certification as a Diplomate of the academy is based upon meeting educational and experience standards, state registration, and satisfactory completion of a written and oral examination. The AIACS 1969 roster lists over 300 persons.

Program specialist

Environmental protection personnel may practice their basic discipline per se or acquire a categorical program expertise beyond their disciplinary specialization. Three examples of categorical program specialists include industrial hygiene personnel, radiation protection personnel, and air pollution control personnel.

Industrial hygiene personnel include engineers, chemists, nurses, toxicologists, physiologists, occupational hygienists, dermatologists, technicians, or similar occupations. Basic industrial hygiene activities include recognizing, evaluating, and controlling those environmental factors which adversely affect health and efficiency of workers in places of employment. These specialists are essentially concerned with four categories of stresses—toxic chemical agents such as dusts, gases, plastics, and pesticides; physical agents or energy stresses such as excessive noise, temperature extremes, and radiations; biological hazards such as infectious agents and enzymes; and other work-related stresses such as monotony, rigors of work process, and equipment design.

In federal agencies and in large industrial companies, these personnel may also conduct research studies on toxicity of materials, analytical methods, and field instrumentation. In such organizations, occupational health programs may also be staffed with physicians, nurses, toxicologists, x-ray technicians, and laboratory personnel offering a comprehensive preventive health program for workers. Industrial hygiene personnel in state and local official agencies provide various consultation and technical services to workplaces within their jurisdiction.

The latest estimate available indicates that nearly 1700 industrial hygiene personnel are employed by manufacturing and other industrial and commercial enterprises, insurance companies, universities, federal agencies, and state and local agencies.

Major professional associations concerned with industrial hygiene are the American Industrial Hygiene Association (1650 members in 1969), the American Conference of Governmental Industrial Hygienists (1065 members in 1969), and the Occupational Health Section, American Public Health Association (700 members in 1969). The first two organizations sponsor the American Board of Industrial Hygiene, an organization established in 1960 to improve the practice and educational standards of industrial hygienists. Certification as a Diplomate of the American Academy of Industrial Hygiene is awarded by the board based upon a system of written and oral examinations. By 1970, the board had certified 570 persons. Certification requirements include graduation with a baccalaureate in chemistry; physics; chemical, mechanical, or sanitary engineering; biology; or other acceptable major subject and eight years full-time employment in industrial hygiene.

Radiation protection personnel at the professional level include health physicists, engineers, chemists, biologists, and other scientific and technical occupations with specialized training. The radiation exposure problems with which they are concerned are associated with electronic products, such as x-ray machines, particle accelerators, microwave ovens, and color television; radioactive materials; and nuclear reactors, as well as environmental radioactive contamination. Their work is conducted principally in industrial, medical, research, or educational institutions that use radiation sources and in governmental agencies that have responsibility for public health protection.

Several professional associations and societies serving radiation protection objectives provide opportunity for membership, such as the Health Physics Society (3000 members); Radiological Health Section (350 members) of the American Public Health Association; American Association of Physicists in Medicine (450 members); and the American College of Radiology. The first three of these serve as sponsors of the American Board of Health Physics, an organization established in 1959 to improve the practice and elevate the standards of health physics. Through a system of written and oral examinations, by 1969 the board had certified almost 500 people as professionally qualified to assume higher level positions in health physics. Requirements for certification include a bachelor's degree in a physical science, or in a biological science with a minor in a physical science, and six years professional experience in health physics (three years of which must have been in applied radiation protection work).

Air pollution control personnel include engineers, chemists, meteorologists, statisticians, physicists, biologists, sanitarians, technicians, inspectors, etc. The principal activities in air pollution control programs are • identifying and measuring chemical pollutants and airborne particulate matter, • measuring and analyzing the meteorological effects on atmospheric pollution conditions, • determining the effects of air pollution on biological systems and inorganic materials, • controlling air pollution sources including industrial production processes, combustion and space heating equipment, and vehicular sources, • developing, installing, and operating a variety of processes and equipment designed to reduce or eliminate the emission of air pollutants, • developing and enforcing air quality and emission standards, and • coordinating and integrating air pollution control efforts with other environmental protection activities and with diverse industrial and governmental programs and agencies conducting activities which affect, directly or indirectly, air quality.

National concern for the air pollution problems has resulted in a major expansion in state, local, and regional control efforts. In 1963, for example, only 11 states had basic air pollution control legislation; by the end of 1970, all 50 had basic statutes. In 1969, there were more than 200 state, local, and regional control agencies. Most control agencies are small in terms of staffing. Fifty percent of the state agencies had fewer than ten full-time positions, and 50% of the local agencies had fewer than seven full-time positions.

The Air Pollution Control Association (5000 members) is the major professional society concerned with air pollution. Other societies including the American Industrial Hygiene Association, American Society of Civil Engineers, American Society of Mechanical Engineers, American Chemical Society, and American Public Health Association are also involved with air pollution activities.

Technician and aide

As environmental protection facilities and services have increased in number and complexity, the need for more trained technicians and aides has become more apparent. The **environmental technician** is an individual prepared for jobs which consist of subsections of work, previously done by professionals (for which full professional training is not necessary); jobs which include new functions supporting the professional that expand the scope of professional services; jobs designed at the entry level so that persons with less than the training or academic credentials that usually accompany professional status can, in relatively short periods, become sufficiently skilled to perform technical tasks; jobs which allow opportunity for individual development, regardless of traditional credentials or other arbitrary status symbols, and permit advancement to duties of greater challenge and responsibilities.

Technicians are utilized in a variety of ways in environmental protection programs. The application of such skills includes, but is not limited to, inspections, surveys, investigations, evaluations, and operation of facilities. Specific tasks may include obtaining appropriate samples of air, water, and food and assisting in tests to determine quality; operating, or assisting in the operation of, water and waste water treatment plants and solid waste disposal facilities; and inspection and evaluation to determine compliance with laws and regulations. Administrative organizations and units which employ technicians are state and local health departments, air pollution control organizations, water purification plants, waste water treatment plants, solid waste collection and disposal units, radiation protection units, consulting firms, and a variety of business and industrial firms concerned with environmental controls. New careers, such as oceanography and meteorology, are continually being developed in environmental protection for technically trained persons.

The number of environmental technicians is difficult to estimate. The 69,500 people employed as technicians in 1970 (Figure 2) occupied positions for which the desirable qualification in training and experience would be those included in the technician definition cited above. In fact, a substantial proportion of the personnel so employed at this time has not had the training or equivalent experience to qualify adequately.

By 1980 the rapid population growth will have created environmental problems requiring 214,000 trained technicians. At the present rate of training—less than 1000 new graduates per year—there will not be enough trained people to meet the demand. Educational facilities and teachers must be updated and added to in significant numbers for the necessary production of trained technicians needed over the next five to ten years.

The **environmental aide** assists professional personnel and technicians in carrying out prevention, control, and service programs. He performs routine tasks under supervision. The aide is usually a high-school graduate and receives on-the-job training in environmental protection activity. An estimated 101,000 aids were employed in 1970 in public water supply, waste water collection and treatment, industrial wastes disposal, solid waste collection and disposal, community sanitation and rodent control activities, industrial safety, air pollution control, and recreational management.

Education and training

The minimum educational requirement for engineers, sanitarians, and many other environmental disciplines is the bachelor's degree. However, in a number of other instances, graduate education is required for disciplinary qualification or for categorical program specialization. In several disciplines the qualifying professional degree is the doctorate.

Most **engineers** now enter the environmental protection field at the bachelor's level, having completed curricula in civil, chemical, or mechanical engineering; however, graduate preparation frequently is a requisite for employment and (or) advancement. Graduate education for engineers in air pollution, water pollution, industrial hygiene, solid waste management, radiation protection, and general practice is offered at more than 100 institutions (Table II). The full range of such specialization is not offered at every institution.

The minimum educational requirement for the **sanitarian** is usually a bachelor's degree with a major in environmental health or in the physical or biological sciences. Presently, 35 academic institutions offer undergraduate four-year programs in environmental health. In 1968, the National Association of Sanitarians (now the National Environmental Health Association) initiated an accreditation program for undergraduate environmental health (or related) curricula.

The minimum educational requirement for the **environmental technician** is an associate's degree, or equivalent, in environmental health, environmental science, radiologic technology, or related areas of specialization. A number of community (junior) colleges or technical institutes offer technical training in these areas.

The **environmental aide** normally is a high-school graduate with varying amounts of on-the-job training, vocational education, and (or) appropriate short-course training in specialized subjects.

A wide variety of short technical courses in environmental subjects is offered by the Environmental Protection Agency and the Public Health Service. In addition to the short courses conducted in the states in response to requests, short technical courses for continuing education are also offered by several other federal agencies and nonfederal institutions.

Ralph C. Graber, *currently detailed to the Office of the Administrator, Environmental Protection Agency, received his BS and MS in sanitary engineering (Pennsylvania State University and Harvard University, respectively). Mr. Graber, with* USPHS *since 1941, was Manpower Director in the Environmental Health Service. He supported education and training programs and development of a national manpower planning system.*

Frederick K. Erickson, *a graduate of the University of Washington (BSCE) and Harvard University (SM), is also assigned to the Office of the Administrator,* EPA. *Mr. Erickson formerly administered the Office of Training and Manpower Development, Environmental Control Administration, with emphasis on national and agency manpower needs and assessing the national supply of environmental control manpower.*

William B. Parsons, *presently with the Office of the Administrator,* EPA, *attended Atlantic Christian College (BA in biology and chemistry) and Yale University (MSPH). Formerly Assistant Manpower Director in* EHS, *Mr. Parsons coordinated manpower training and development programs as well as consulting with institutions on the needs and programs for environmental health manpower.*

Homer J. Hall
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Linden, N.J.

NO_x control from

Nitrogen oxides, major reactants in photochemical smog, may be controllable by various NO_x scrubbing and oxygen-controlling systems

Oxides of nitrogen are receiving increasing attention as air pollutants. Since they are formed from a variety of sources, no simple processes are available either to prevent their formation or to remove them once formed.

The two oxides NO (nitric oxide) and NO_2 (nitrogen dioxide) are commonly lumped together as NO_x. They are easily interconverted in the atmosphere from one to the other, and their ratio changes with the time of day—depending on the action of sunlight, oxygen, and other oxidizing or reducing agents present. These reactions have an important bearing on smog formation under adverse conditions, such as those found commonly in the Los Angeles area, where the participation of NO_x in smog reactions was established in 1952.

NO_x is emitted into the atmosphere in three distinct concentration domains: • as NO_2 and NO in high concentration but small total amounts from nitric acid or nitration processes, • as NO (plus small amounts of NO_2) in intermediate concentration but large total amounts in the emissions from fossil fuel combustion, and • as NO_x in the ambient atmosphere in low concentrations but very large total amounts from the natural biochemical nitrogen cycle. These sources have different but closely interrelated effects on the whole problem of NO_x control and the technology necessary to accomplish it.

NO_x sources and control

Pure NO_2, a toxic irritant gas, is valuable as a chemical raw material for the manufacture of nitric acid. It is produced commercially by oxidizing ammonia in air or oxygen to NO, which is further oxidized to NO_2, and reacted with water to produce nitric acid. This reaction forms NO which is returned to the cycle:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$2NO + O_2 \rightarrow 2NO_2 \rightleftarrows N_2O_4$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The nitric acid produced is absorbed in water, and the process tail gas contains approximately equal concentrations of NO and NO_2. The concentration limit for economical NO_x recovery from this tail gas varies with plant size and efficiency—from about 1000 to 10,000 parts per million (ppm) before treatment for abatement. For much lower emission levels the value of the NO_x recovered is less than the cost of absorption, making it cheaper to remove or destroy the remaining gas without trying to recover it. The term *abatement* is used in this article to refer generically to chemical or physical removal of pollutants from a process effluent stream.

Most of the abatement research on NO_x has involved pure sources, specifically the tail gas from nitric acid manufacture, which differs substantially from the problem of NO_x abatement from other sources. On the positive side, there is a direct payout for any recoverable NO_2, which is free of impurities and can be reused in the process without introducing extra equipment or process steps. Also, there is a strong incentive to minimize the venting of NO_2—easily detectable by its color and irritating odor. However, the absence of other gases or vapors as impurities is important.

Substantial progress has been made in the abatement of NO_x from nitric acid production, and processes are under development to reach still lower levels. This source, however, is cur-

stationary sources

rently 1% of all man-made NO_x emissions. Even at the same high concentration level, new research is required to develop NO_x abatement processes applicable to mixed or impure effluent streams.

The fumes from organic nitrations contain NO_x in amounts and ratios comparable to those in the tail gas from nitric acid manufacture, but this vent gas may also contain substantial amounts of free oxygen, other acid gases, hydrocarbon residues, or all of them together. The NO_x present can be chemically reduced only by consuming all oxygen (a minor constituent in nitric acid tail gases), or oxidized by oxidizing all hydrocarbons, or neutralized by reducing the acids present. Engineering and economic limitations complicate the process. For example, the catalytic reduction of NO_x from nitric acid tail gas with methane releases large amounts of heat which can be tolerated by an expensive special catalyst. But the useful life of both the catalyst and the reaction system (including a turbine for the recovery of heat energy) can be critically shortened if higher temperatures are caused by significant amounts of oxygen or other oxidizing agents.

NO_x also appears as a by-product of any fossil fuel combustion process in air. The emission level from stationary combustion sources is commonly 50 to 1000 ppm, although higher values of 1500 ppm or more have been observed under severe conditions of high flame temperature and low heat transfer rates.

Combustion accounts for over 95% of the man-made NO_x released to the atmosphere, with roughly half from internal-combustion engines, mobile or stationary, and the rest about equally divided between power plants and industrial, commercial, and domestic heating. A split between the estimated outputs of NO_x from these major types of sources during the years 1950–2000 is shown in Figure 1. (For details see reports in additional reading.)

The estimates and forecasts shown are for median trends and assume the continuation of current practices, i.e., with minimum levels of NO_x control. For the foreseeable future, stationary sources are expected to contribute over half of the total NO_x emissions nationwide. This trend will probably be emphasized by current legislative action on the control of motor vehicle emissions. Within stationary sources, electric generation is estimated to account for 25% of NO_x emissions in 1950, growing to 34% in 1960, 38% in 1970, and 47% in 1980. The increase in the contribution of electric generation to NO_x would be even more rapid except that nuclear power which (with hydropower) accounted for 17% of the gross energy input to electricity generation in 1965, is projected to increase to 29% by 1980, and 60% by the year 2000.

Almost all of NO_x from combustion is released initially as NO, not NO_2. The NO is metastable at ambient conditions; it can be oxidized fairly easily to NO_2 but this requires time and energy. Most processes for the abatement of NO_x in combustion stack gases are ineffective for NO in the absence of NO_2, and those which show promise are only in the laboratory or conceptual stages to date.

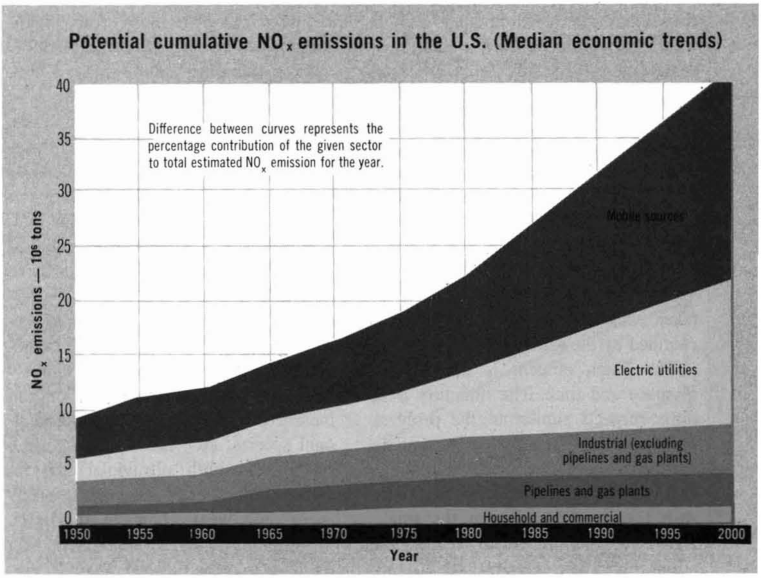


Figure 1

Realistically, NO_x abatement from combustion flue gases with conversion of this pollutant to useful by-products is envisioned only as incremental to a potential flue gas desulfurization process. More success has been achieved in the modification of combustion processes to minimize the amount of NO_x produced.

The chemistry of NO_x in air, from a combustion process or any other source, is complicated by the fact that NO and NO_2 are both oxidizing and reducing agents. Also, the interconversion of these two compounds is controlled by kinetics and not by chemical equilibrium. The very strong effect of temperature on the formation of NO and its equilibration into N_2 and O_2 means that time–temperature profiles are a major factor in NO_x production—scale-up factors are important and extrapolations uncertain. Actual data on large-scale operations are required to confirm predictions made on the basis of theory or smaller scale experiments.

Problems in process research

The emission factors available to estimate the amounts of NO_x released from a number of sources are not reliable. The uncertainties are serious enough that the whole concept of using an emission factor instead of actual measurements is suspect, and much better data are needed before such estimates can be applied for single installations. Many of these factors are based on the literature from spot measurements which are not valid because they ignore the changing character of the effluent from a batch process. Some batch processes are considered as large sources of NO_x, such as the open burning of garbage or forest fires. The maximum concentrations observed in such a combustion process may occur for only a short period in a long burning time. On the other hand, small-scale tests are ineffective for determining the effects of increasing severity when the same burning process takes place at a point completely surrounded by the same type of burning.

The batch effluent is nonuniform in space and time. The difficulty is in some respects similar to the problem of how to sample properly particulate matter in a large stack, where loadings and gas velocities both vary markedly with time and location in the stack. Also, secondary reactions which have a major effect on NO and NO_2 are affected strongly by time–temperature profiles within the variable combustion zone. These systems are too large to collect a total sample, so the best present approach has been collecting a series of samples at a traverse across the effluent stream, and averaging these over a period of time. Equivalent or better information will result only when it is possible to take a single measurement across the stack or other source—either at the source or from a remote instrument which can see through and measure the total stack or source stream. The same principles and hopefully the same instruments should be applicable to the measurement of off-gases from a garbage dump or from a forest fire.

The reactions between NO and NO_2 become even more important in the ambient atmosphere. The natural nitrogen cycle introduces NO_x into the atmosphere at a concentration of several parts per billion, where it performs vital functions as a source of nitrates in rainfall to fertilize vegetative growth. This concentration is low compared to the range of 0.05 to 0.1 ppm (annual average) which characterizes many urban environments, but it represents a much larger total amount. This fact is sometimes set aside in discussions of NO_x control, since air pollution is primarily a problem of the interaction of pollutants and people where both are present in large concentrations. It does have a bearing, however, in special situations such as NO_x release in remote areas. One example is a rural pipeline pumping station surrounded by farmers using ammonia to fertilize their crops. While the engines driving the compressors in such a pumping station may release significant amounts of NO_x, much of this will be converted in the atmosphere to nitrates in rainfall and dusts. Both economic and social questions are involved in deciding whether it is desirable to treat these particular NO_x emissions as pollutants to be removed at considerable expense in an area of minimal population exposure.

The complex interrelationships between NO and NO_2 have also complicated the development of satisfactory field instruments for the detection and measurement of NO_x. The predominant species, NO, has relatively weak spectra (in both ultraviolet and infrared ranges) not free of interferences, and weak chemical reactivity. More importantly, when chemically oxidized to NO_2, this NO_2 may decompose to NO and an oxygen atom, which is sufficiently active to react with atmospheric nitrogen and create more NO. The result may be a reading which is artificially too high. At the same time, sulfur dioxide in large amounts can readily reduce NO_2 to NO, in the presence of moisture, so reactions between interfering gases during the course of the analysis are a common problem. This situation presents a strong incentive for completing the development of direct methods of analysis for NO and NO_2 in the original sample, without any pretreatment or conversion steps during the analysis.

Control of stationary source emissions

The data supporting Figure 1 show the following ranking for stationary NO_x emission sources:

- Electric power plants.
- Industrial combustion sources.
- Stationary internal combustion engines, used in pipelines and gas plants.
- Domestic and commercial combustion equipment.
- Noncombustion sources.

The release of NO_x in combustion gases can be minimized in many of these operations but not entirely avoided by combustion process modifications. Many different modifications are possible, separately and in combination, and the optimum control system will vary with the type of service. Much work is necessary to perfect these, especially for any small-scale use. Domestic and small industrial plants which operate under less severe conditions should be amenable to the same procedures, but high costs will be difficult to avoid since they do not normally have suitable operating controls. Combustion modifications have had some success with large oil- and gas-fired units, but the question remains of how much can be done to avoid NO_x formation in burning coal—a major part of the problem.

The most promising methods of combustion modification identified to date are low excess air firing, staged combustion, "off-stoichiometric" firing, flue gas recirculation, water injection, and, particularly, combinations of these techniques. The important design features are burner configuration, location and spacing, and the types of firing and combustion methods used.

Low excess air firing is well documented as effective for gas and oil combustion. No test data are available for commercial coal firing equipment.

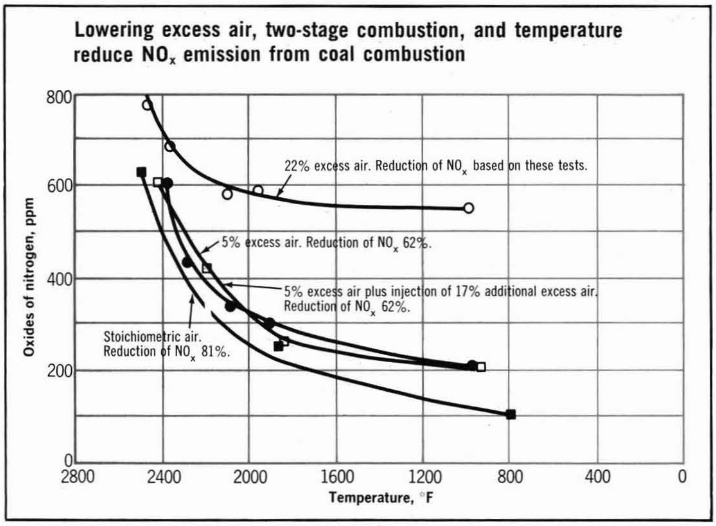


Figure 2

However, laboratory data show the potential of this technique if problems involving complete fuel burn-out and heat transfer surface corrosion can be overcome (Figure 2). With coal, low excess air can easily result in an unburned fuel increase, unless careful controls are maintained.

Two-stage combustion consists of firing all fuel with substoichiometric quantities of primary air in the first stage, say 90–95% of the theoretical requirement, and injecting secondary air in the second stage to complete fuel burn-out. In the first stage, NO formation is limited by the unavailability of oxygen. Removal of heat between stages reduces the temperatures achieved when the excess air is added, thereby kinetically limiting NO formation. Reductions as high as 90% have been achieved by combining this technique with low overall excess air firing in a large gas-fired power plant. The application of this technique to coal firing (Figure 2) is expected to raise problems similar to those encountered with low excess air firing alone. "Off-stoichiometric" firing which uses alternating fuel-rich and fuel-lean burners is a variant optimization of staged combustion.

Recirculation of flue gases lowers the peak flame temperatures by diluting the primary flame zone with recirculated combustion flue gases. The oxygen concentration is also lowered, which favors reductions in NO_x emissions. (The effectiveness of this method is illustrated in Figure 3.) Recent data obtained with a tangentially fired electric utility boiler burning gas indicate that NO_x emissions can be lowered by 50% (from 300 to 150 ppm) using this technique. Injection of low temperature water or steam is similar in concept to flue gas recirculation—thermal dilution of the flame can be achieved, resulting in reduced NO_x emissions. This technique appears to have limited utility for NO_x control for furnaces because of operating debits. However, laboratory studies show it to be very effective for the reduction of NO_x emissions from internal-combustion engines, apparently without affecting the cycle efficiency.

The combination of combustion modification techniques, demonstrated both in full scale and laboratory equipment, appears to be the best approach to NO_x control. Examples of this concept are the combination of low excess air firing with a modified version of two-stage combustion; low excess air firing with flue gas recirculation; tangential firing with flue gas recirculation and other improvements on the two-stage combustion techniques, such as "off-stoichiometric," resulting from supplying some burners with fuel-rich, and others with fuel-lean mixtures.

As for design features, variations in NO_x emissions have been observed with different burner types. The highly turbulent operating features of cyclone burners, for example, can result

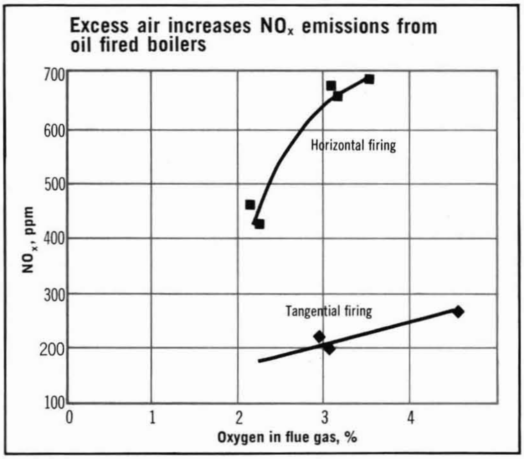


Figure 3

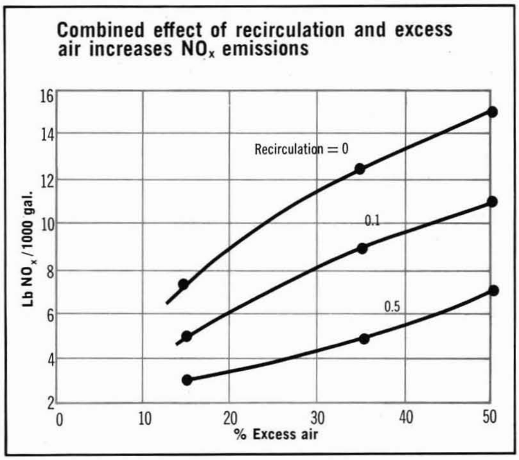


Figure 4

in high levels of NO_x emissions in coal-fired power plants. On the other hand, in tangential firing where the furnace itself is used as the burner, as much as 60% reduction in NO_x levels has been reported (Figure 4)—presumably, due to the lower peak flame temperatures resulting from spreading out the flame front.

Lower flame temperatures are also the basis for considering fluidized bed combustion for low NO_x emission boilers. This technique, actively being researched both in this country and abroad, consists of combusting the fuel in a fluidized bed of solids containing part of the heat transfer surface. The very high heat transfer rate characteristic of this system enables maintaining low average combustor bed temperatures, typically 1500–1800° F. In fluidized bed combustion of fuels such as coal, however, the oxidation of chemically bound nitrogen in the fuel may result in emissions exceeding those formed by the atmospheric nitrogen fixation in conventional combustion, and further modifications, such as gasification followed by secondary combustion, may need to be developed.

Methods of abatement making it possible to remove NO and the relatively small amount of NO_2 which accompanies it in the stack gas from a coal-burning power plant would be highly desirable, but there is no such system commercially available. The known adsorbents or absorbents for NO_x have a low capacity, NO_x concentrations are low, and enormous vessels are required for separation processes. Known catalytic decomposition and reduction systems are inadequate to cope with dilute stack gases. The low reactivity of NO means that some two-stage process is required to produce NO_2 for adsorption, or for absorption plus reaction with NO to produce N_2O_3 (the reactive species) if a chemical reaction is to be involved.

Flue gas treatment processes can be considered in the following general categories: catalytic decomposition of NO_x, catalytic reduction of NO_x, physical separation of NO_x from the other components of the flue gas, adsorption of NO_x by solids, and absorption of NO_x by liquids. Particular attention has been given to processes potentially capable of controlling SO_x emissions as well.

While the thermodynamically favored decomposition of NO would provide a comparatively simple method of controlling emissions, no catalyst has been found which provides sufficient activity at reasonable temperatures (even though there has been considerable research in this area on automotive emission controls).

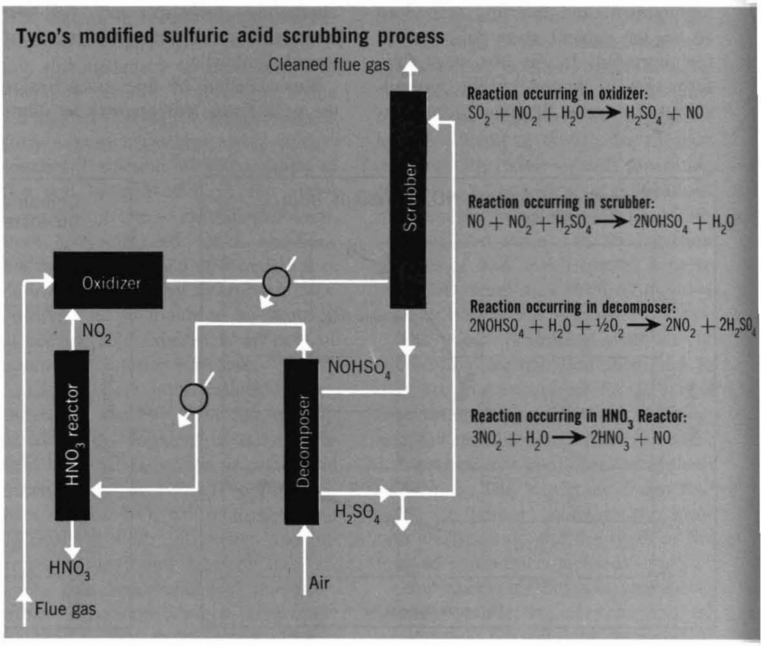
Nonselective reduction under net reducing conditions has been applied to the control of nitric acid tail gas emissions with mixed success. Noble metal catalysts are used with such reductants as CO, H_2, and CH_4, but supported copper oxide may also be effective. Even with such a relatively inexpensive catalyst, a nonselective reduction process does not appear to be practical. The requirement for net reducing conditions means that either the combustion must be carried out under substoichiometric air conditions, or that CO, H_2, or CH_4 must be added to the flue gas upstream of the catalytic reactor. Either approach would result in some emissions of these gases and(or) in an overall decrease in plant thermal efficiency.

In the case of selective reduction, ammonia is known to be capable of reducing NO selectively in an oxygen-containing environment. Such NO_x reduction with NH_3 has been practiced to a limited and rather unsuccessful extent in nitric acid plants. The potential attractiveness of ammonia for flue gas NO_x reduction is that it might also control SO_x emissions in a combined process. This reaction would require temperature control and a catalyst which is not yet available.

NO_x removal from flue gases based on differences in such physical characteristics as molecular size, condensation temperature, and magnetic susceptibility of the components was investigated. Unfortunately, the physical properties of NO fall within the range of properties of the other, more abundant, components of the flue gas. Investment and operating costs for physical separation techniques were judged to be prohibitive.

All common adsorbents were considered as potential candidates for removing NO_x from flue gas. Among solid sorbents, certain metal oxides, particularly manganese and alkalized ferric oxides show technical potential, especially in conjunction with a regenerative system with recycle of NO_2 into the flue gas. However, sorbent attrition under the severe conditions required for flue gas treatment is a major technological stumbling block for developing such processes.

Of all the potential flue gas control techniques, aqueous absorption systems using alkaline solutions or sulfuric acid appear the most promising for combined control of nitrogen and sulfur oxide emissions. Various organic


Tyco's modified sulfuric acid scrubbing process

Reaction occurring in oxidizer:
$SO_2 + NO_2 + H_2O \longrightarrow H_2SO_4 + NO$

Reaction occurring in scrubber:
$NO + NO_2 + H_2SO_4 \longrightarrow 2NOHSO_4 + H_2O$

Reaction occurring in decomposer:
$2NOHSO_4 + H_2O + \frac{1}{2}O_2 \longrightarrow 2NO_2 + 2H_2SO_4$

Reaction occurring in HNO_3 Reactor:
$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$

Figure 5

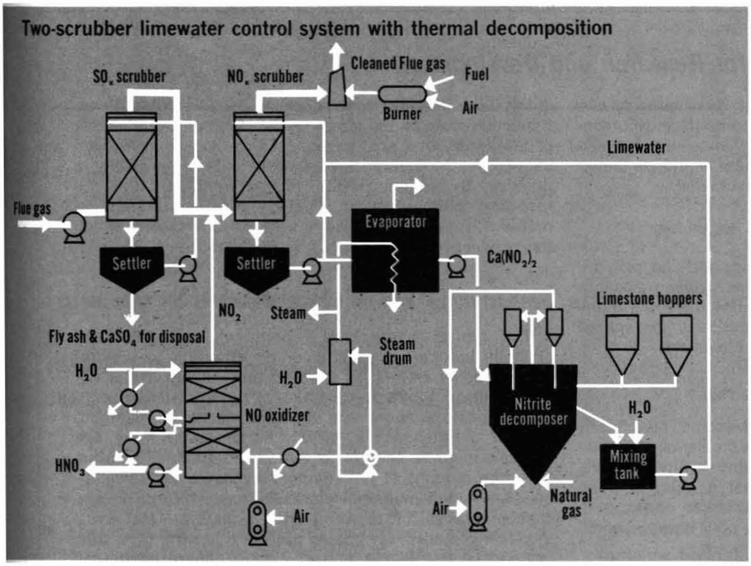


Figure 6

and inorganic complexing solutions that dissolve NO were considered for its control, but were judged to have too little capacity, to degrade too easily, to be too volatile, or to cost too much. Using alkaline solutions or sulfuric acid for control of nitrogen oxide emissions requires achieving equimolar concentrations of NO and NO_2 in the gas, since absorption of the combined oxide, N_2O_3, is the most favorable.

Different ways of achieving such equimolar concentration in the flue gas have been considered in detail. Known homogeneous or catalytic oxidation techniques are too slow or costly for achieving such equimolar concentrations. The recycle of NO_2 into the flue gas appears to offer the best possibility and may be accomplished by oxidizing the concentrated NO stream produced by thermal, catalytic, or chemical regeneration of the spent absorbent. Aqueous alkaline absorption systems based on discarding spent absorbent are becoming unacceptable in most locations, because they may create a significant water pollution hazard.

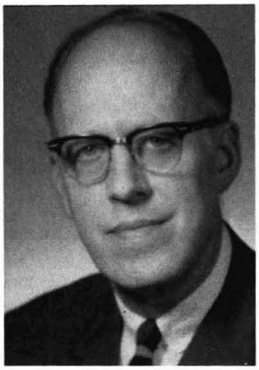
The modified lead chamber acid process being studied by Tyco Laboratories under contract to the Air Pollution Control Office (formerly the National Air Pollution Control Administration) recycles NO_2 to oxidize SO_2 to sulfuric acid mist and to form the N_2O_3 absorbed by the acid (Figure 5). The fact that this process requires the recycle of NO_2 to oxidize the SO_2 to sulfuric acid, in addition to forming N_2O_3, places very stringent requirements on scrubber efficiency for N_2O_3 recovery.

Among alkaline scrubbing systems considered, those utilizing limewater and magnesium hydroxide solutions show the best potential for abatement of SO_2 and NO_x emissions (Figure 6). Since oxidation of SO_2 to sulfuric acid is not required nor even desirable in such processes, in contrast to the Tyco process, the requirements for recycle of NO_2 and high scrubber efficiency should be greatly reduced. Compared to limewater, a magnesium hydroxide scrubbing solution offers the potential advantage of easier oxide regeneration from both the sulfite and the nitrite formed in the scrubber. However, the problem of avoiding the consumption of recycle NO_2 for unwanted SO_2 oxidation must be solved.

Alternate methods of recovering energy from fuels which do not result in high levels of NO_x production in the initial process are possible. This will be true for fuel cells, for example, but it is not necessarily true for all noncombustion processes. Any electric arc or other hot process such as MHD (magnetohydrodynamic electricity generation) which exposes air to extreme temperatures can create substantial amounts of NO_x from N_2 and O_2, regardless of whether the process involves combustion or not. The possible bearing of such processes on problems in NO_x control remains to be determined.

Research in NO_x control techniques

William Bartok, *research associate and project director of Esso's APCO-sponsored studies of stationary NO_x emission control, has been with Esso Research and Engineering Co. since 1957. He received his B. Eng. in chemical engineering and a Ph.D. in physical chemistry from McGill University. Dr. Bartok has been working in the research fields of combustion studies and air pollution control.*



Homer J. Hall *is information research associate, Esso Research and Engineering Co., Linden, N.J. Dr. Hall, a graduate of Ohio State University (Ph.D. in organic chemistry), has worked in the area of air pollution control since 1968. He has had experience as head of hydrocarbon separations, technical secretary of the Esso patent committee, and senior analyst and editor in the Technical Information Division.*

is also needed to confirm present theories as to how NO and NO_2 are formed in combustion, from N_2 and from N in the fuel, and how they are subsequently transformed by reactions with other species present and with each other. A substantial body of such knowledge, with a good theoretical basis, is ready for confirmation or modification based on further experiments.

Areas of Special Opportunity for Research and Development

A number of engineering and research developments can be pinpointed as areas of special opportunity in NO_x control. Some of these, based on experience, are promising, others are doubtful. But all of them would be immediately useful if good answers can be obtained:

Optimization of combustion research technology

This is a problem of many variables with no one answer. It is necessary to determine where a given procedure should and should not be applied, since there are many instances where a control method practical under special circumstances may be uneconomical elsewhere.

How to minimize NO_x emissions from coal

Combustion modifications are troublesome, particularly reduced excess air which may create problems of incomplete burnout, corrosion, and possible safety hazards. The effect of fuel N content may set a lower limit on NO_x production with coal (and to a lesser degree with some fuel oils). Coal burning requires both basic research and applied testing to get definite answers.

Catalytic decomposition of NO to nitrogen and oxygen

Remote as the chances are, because of reaction kinetics and the lack of any positive results after intensive experimentation, the fact remains that NO is thermodynamically unstable at ambient conditions. It should be decomposable into its elements but no leads are available. Any economic process to accomplish this would be a real breakthrough.

Selective NO_x reduction in the presence of excess oxygen

The chances of accomplishing this are also doubtful but such a process will be highly useful if it can be found. Economics and engineering difficulties include the lack of practical catalysts, a penalty in thermal efficiency, large vessels and large gas volumes required for treatment. These now prevent the application of this technique except under special conditions.

Complete development of an absorption–reaction system

The feasibility of an absorption system which can convert NO_x in a flue gas to reactive N_2O_3 and thus remove it from the effluent remains to be established, both on the bench scale and in larger test applications. The effects of SO_2 (and other acid gases) on this system have been allowed for in theory, but are still to be determined in practice. By-product credits derived from NO_x and SO_2 recovery could offset anticipated large capital requirements. No present promise is seen for any system which has a selective affinity for NO, in the absence of NO_2.

Low-cost control package for small/intermediate furnaces

The typical homeowner, apartment superintendent, or small industry gives little or no attention to his furnace or boiler as long as it keeps the heat up. He is not technically competent to make any adjustments whatever in its operation, and the amount he is willing to pay for maintenance is strictly limited even if he can realize a definite savings in fuel consumption. Nevertheless, the amount of NO_x emitted by domestic, commercial, and small industrial plants is large, second only to mobile sources and power plants as part of total emissions. A remedy will require the development of a truly low-cost control package, as nearly automatic and foolproof as possible.

Reliable and rugged instruments for both NO and NO_2

This area has been the subject of intensive current research, and there are indications that most of the problems recognized in NO_x instrumentation can be solved. The instruments available and now foreseen are expensive to buy or operate, and simpler or cheaper equipment is very desirable.

Data on the NO_x balance among source emissions, ambient concentrations, and rates of disappearance from the atmosphere

NO_x is produced in all combustion processes; its fate is influenced strongly by sunlight, wind, and rain. Amounts ordinarily dissipated in the atmosphere may become critical under adverse conditions. These variables involve relationships among reaction times, concentrations, and effects which are only partly defined. Much better data are needed for an understanding of these relationships, since they may have an important bearing on the degree of NO_x controls required.

Acknowledgment

The authors wish to acknowledge important contributions made by other members of the NO_x study team at Esso Research and Engineering Co., including Messrs. Allen R. Crawford, Alan R. Cunningham, Erwin H. Manny, and Alvin Skopp.

This study of NO_x control was based on work completed under National Air Pollution Control Administration contract no. PH 22-68-55. (currently the Air Pollution Control Office of the Environmental Protection Agency).

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current
research

Diffusion of Aerosols Released Upwind of an Urban Complex

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■ The results of a field program to measure the dispersion of a tracer material in the vicinity of an isolated urban area are described. Tracer material released as an aerial line source was sampled at 250 surface sites and by vertical arrays on one 700-ft tower and on a 1500-ft balloon tether. The enhanced surface roughness and thermal mixing caused by the city produced a 30 to 50% increase in the vertical mixing of the aerosol over the city as compared with the adjacent rural pattern in the urban area. The centerline (axis of maximum concentration) of the vertical profile of the tracer cloud appeared to be translated to the ground at a rate governed by the vertical temperature structure of the rural atmosphere. Average surface dosage patterns suggest a cellular or helical motion in the wind field near the city.

A major effort to observe and analyze the dispersive capacity of the atmosphere was conducted at Ft. Wayne, Ind., from 1964 to 1965. This project, labeled the Urban Diffusion Project (Hilst and Bowne, 1966), was designed specifically to determine the manner in which an isolated city affects the structure of atmospheric motions and thereby the manner in which airborne materials are diffused and transported over and through the city. Knowledge of the differences in dispersive capacity is important at this time of increased public concern with air pollution. The National Air Pollution Control Administration requires Air Quality Regions to consider modeling the atmospheric diffusion in their regions as part of their plan of action to abate local air pollution. Information gathered previously on dispersive rates in the atmosphere has been obtained in rural areas.

In approaching this problem it was realized that the major effects of the city should be apparent in vertical diffusion of airborne material. The surface roughness and the thermal inhomogeneity—*i.e.*, the heat island effect—which characterize the city affect most strongly the vertical structure of turbulence and the atmospheric stability. For this reason, and in an effort to isolate these effects from horizontal inhomogeneities, a quasi-instantaneous line source of a tracer material was disseminated from an aircraft flying upwind from the city and along the line normal to the mean wind direction at the time of release. To provide a control measurement against which the effects of the city could be judged, a surface sampling network was established in an adjoining rural area. This auxiliary network of measurements of surface dosage also provided data for comparison with other experimental results in rural areas with different types of tracer release.

A city is not homogeneous with regard to surface conditions. Residential, park, industrial, and commercial zones have their own characteristic surface roughness and thermal properties which could produce significantly different effects on atmospheric motions in the city. All of these considerations led to the experimental design described briefly in the next section.

Experimental Design

The need for vertical measurements of atmospheric parameters and tracer distributions demanded the most attention, and led to the greatest operational difficulties. The starting point for the experimental design was the measurement of the surface dosage patterns in the city and in the rural control zone, and its major components were: the surface meteorological sensor network, the vertical arrays of meteorological sensors, the surface tracer dosage network, the vertical tracer dosage arrays, the tracer release aircraft, and the meteorological sensor aircraft. The sampling arrays are shown in Figure 1.

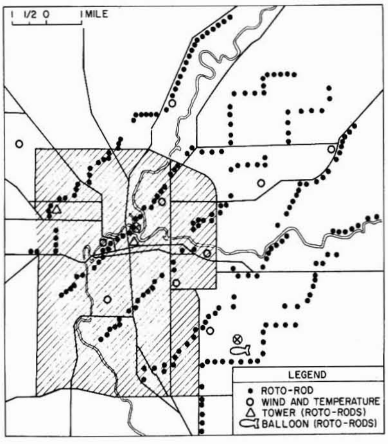

Figure 1. Experimental network at Ft. Wayne showing locations of tracer sampling and meteorological measurement stations

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Meteorological and tracer sampling in the vertical was accomplished at the 244-m WANE-TV tower northwest of the city and at the 61-m General Telephone relay tower in the center of the city. In addition, two wiresondes and one modified radiosonde were used to obtain vertical temperature and wind measurements within and downwind of the city. Vertical tracer sampling was also done on a farm southeast of Ft. Wayne (Figure 1).

The surface dosage pattern was established by five crosswind lines of surface samplers. The rural network was an extension of the urban network. Thus, a total of 50 stations along each line, or 250 altogether, constituted the basic surface dosage network. Additional information on the time of arrival and departure of the tracer cloud was obtained by 25 sequential-filter samplers distributed more or less randomly throughout the sampling network.

It was recognized that the diffusion history of a single, initially small, cloud of tracer material could only reflect the atmospheric motions in its immediate vicinity and that these motions might vary significantly between clouds, released only seconds apart. To measure this internal variability of diffusion rates, two sequential releases of tracer materials with distinctly different fluorescent colors were made. A second release of two tracer clouds was made after the rotorod sampling device had been automatically adjusted to measure the resultant dosages separately. This automatic sequencing of the rotorod samplers was done by a rotation-reversing switch attached to a mechanical timer on each rotorod. The first two tracer releases were sampled on one face of the rod, the second two on the opposite face.

The tracer technique used was developed by the U.S. Army Chemical Corps (Leighton, 1955) to provide a uniquely identifiable tracer for use in studying diffusion in the atmosphere. The fluorescent materials used in this program were finely ground powders of zinc-sulfide and zinc-cadmium-sulfide. The materials appear yellow or green under ultraviolet light. Materials used were prepared by the U.S. Radium Corp. The yellow pigment (USRC Lot H-395) had a mass mean diameter of 3.3 μ, and yielded 1.32×10^{10} particles per gram. The green pigment (USRC Lot H-396) had a mass mean diameter of 3.2 μ, and yielded 1.45×10^{10} particles per gram.

The tracer material was collected on a rotorod sampler. The rotorod is an impaction device made in an H-shaped $60 \times 30 \times 0.38$ mm chromel ribbon coated with high-vacuum silicone grease. The nominal sampling rate is 41.3 liters/min when rotated at 2400 rpm. The average collection efficiency in winds less than 15 m/sec is 63%, yielding an effective sampling rate for the particle size used of 26 liters/min. A lot is rejected for tracer studies if more than 1% of the mass is contained in particles less than 1 μ or larger than 10 μ. Particle-size distributions are log normal.

Results

The major features of surface dosage in and around Ft. Wayne are shown in Figure 2, which shows the average dosage at each of the surface stations for all trials. Two significant features should be noted: the maximum average dosage occurs in the rural area adjacent to the city; and the maximum dosage in both the city and rural areas occurs at the first sampling line; dosages decrease rather regularly from the upwind to the downwind edge of both sampling areas. There are no significant indications of isolated patches of anomalously high or low dosage in either area.

Figure 2 is a composite picture of surface dosage and, as such, represents the expected dosage pattern over many repetitions of aerial line releases. The variability from one trial to another may be measured in several ways and most of the present analyses are, in fact, devoted to the understanding of these variabilities and their causes. However, one general statistic which may be applied is the variance among the entire set of experimental trials of the dosage measured at each station.

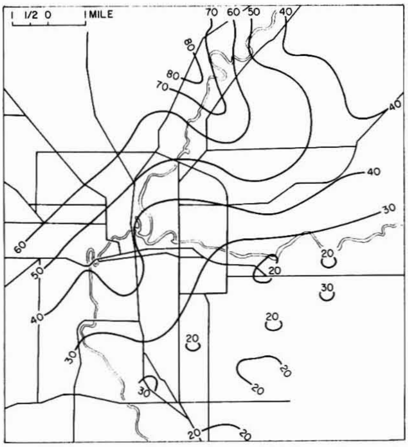

Figure 2. Average surface dosage (particle-min/liter) observed in Ft. Wayne and adjacent rural area. Note distinctive tongue of maximum dosage over rural area

The distribution of individual trial values of dosage at a single station is strongly skewed toward high values of dosage. This distribution is limited to a lower value of zero, no exposure in a single trial, but ranged upward to the order of 1000 particle min/liter. Because of this skewed distribution the variance of dosage or the square root of variance, the standard deviation is not a good measure of variability among trials. There is a strong variability among individual station exposures in any one trial, but we must conclude that these variabilities are random in nature and are not associated with variations of land use, structures, and the like. There are significant differences between dosage values measured in the city and in the rural areas and there is a transition zone between the city and the country, but otherwise, the variability of dosage values between pairs of stations equidistant from the release line in any one trial is largely random, and this random variability sets the lower limit for predictability for individual station dosage values. Since the analysis of composite dosages over all trials showed no regional anomalies of dosage within the city or rural areas, a 10-station array in the central portion of each sampling line in each of these two areas was chosen for the detailed analysis of each trial. The average and standard deviation of dosage for each 10-station group were calculated, giving an average exposure value for each sampling line in the city and in the rural area.

The average dosage in the city and rural areas varied through three orders of magnitude. The variation of dosage among the 10 stations in single trial ranged from 25 to 50% of the average dosage, when the average was relatively large to the value of the average dosage itself when the dosage was relatively small. It seems that the random variability mentioned previously is about a factor of two; that is, the estimate of average dosage is within a factor of two of the individual station dosage about 90% of the time.

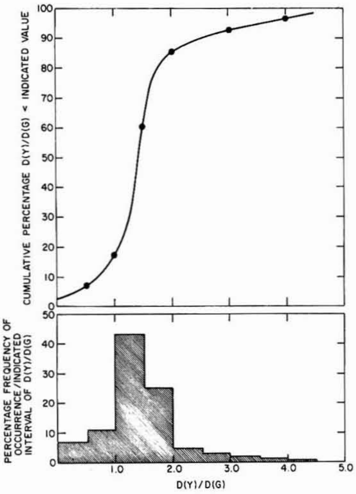

Figure 3. Comparison of ratios of total dosage for near simultaneous release time and position

In 14 trials, sequential releases of yellow and green pigment were made along identical flight paths within 5 to 15 min of each other. The yellow pigment was always released first. A comparison of the average dosages caused by these pairs of tracer releases is shown in Figure 3, where the frequency of occurrence of average dosage ratios for the first release D(Y) and the second release D(G) is shown. These comparisons show that the ratio of average dosages, D(Y)/D(G), may range from 0 to about 4. Further, Figure 3 suggests that the first release produced dosages generally in excess of the dosages produced by the second release. This result, that even the average dosage may vary significantly from one tracer cloud to another under identical gross meteorological conditions, implies that an analysis aimed at separating the meteorological variabilities which cause variations of the transport and diffusion of individual tracer clouds must take into consideration variabilities in the meteorological conditions over the short-term.

As an example of the measurements made, a complete graphic portrayal of the tracer and meteorological measurements made in the vertical plane through the city and by surface networks during a single trial are shown in Figures 4 to 6. The data are for trial 65-02G2, the case that produced the maximum average dosages in both the city and rural areas. Study of these pictorial presentations points to several important features which only such complete measurements could reveal. First, there is the indentification of the trajectory of the cloud axis and the vertical distribution of the tracer cloud as it entered and left the city (Figure 4). This measurement has contributed most to the understanding of the generation of a diffusion anomaly by the city.

The second important feature is the surface dosage pattern which must be synthesized with the vertical profiles to provide the realistic three-dimensional picture of dosage which is by far the most direct and sensitive indicator of air movement and dispersion over the city.

After all valid trials had been assembled in the form shown in Figures 4 to 6, the patterns of vertical and surface dosage were examined for similarities. Those trials for which vertical data were lacking were considered in a separate group which also contained nine other trials to provide a verification base.

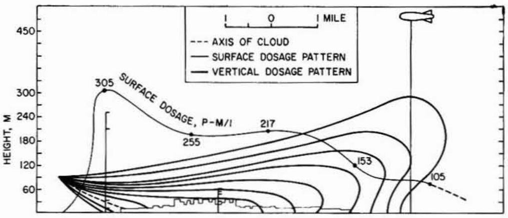

Figure 4. Vertical distribution of dosage observed during trial 65-02G2 and the accompanying surface dosage pattern. Note translation of the tracer cloud axis to the ground

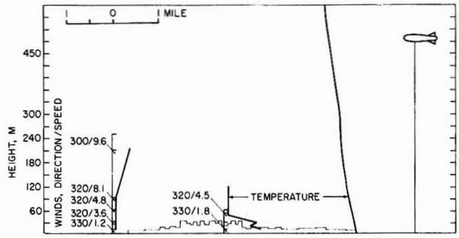

Figure 5. Vertical temperature and wind profiles observed during passage of tracer cloud for trial 65-02G2

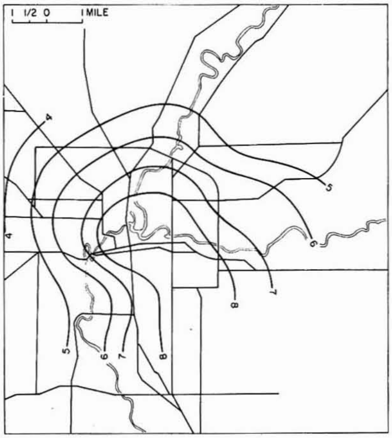

Figure 6. Surface air temperature pattern in °C

Inspection of the vertical dosage profiles and the accompanying surface dosage patterns revealed that each of the individual trials could be classified into one of four categories, depending primarily on the shape of the vertical dosage profile at WANE. These four categories are shown in Figure 7, and may be described qualitatively as follows.

Class 1. The tracer cloud remained totally above the ground level. The vertical profiles at the downwind and the upwind edges of the city showed a clear axis of maximum concentration and the top and bottom of the cloud. The surface dosage was zero throughout the surface sampling network.

Class 2. The cloud axis was brought slowly to the ground and reached the ground level within the sampling network. The upwind vertical dosage profile showed a distinct maximum above ground level.

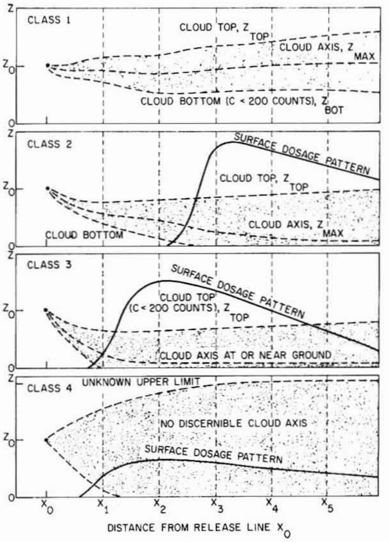

Figure 7. Geometric basis for classification of dependent trials; x_1, x_2, . . .x_5 are surface sampling line positions

Class 3. The tracer axis was translated quickly downward so that it was at, or near, the surface as the cloud entered the city. The vertical profile of dosage at WANE showed a distinct bell shape, with the maximum near the ground and a cloud top as measured by dosages going to near zero at or below the top of the sampling array. The surface dosage pattern showed the maximum at the upwind edge of the city.

Class 4. The cloud was thoroughly mixed in the vertical dimension by the time it arrived at the upwind edge of the city. This class was identified by near-uniform dosages over the height of the vertical sampling array at WANE and by relatively flat and small surface dosage patterns and magnitudes. No cloud axis was discernible in these cases.

Several interesting descriptive features emerged from the data and may be seen in Figure 8. For one, the average city rural dosage values have been clearly separated into overlapping but distinct ranges by the classification procedure. The average and range are shown by class number; clearly, the largest values of dosage and the greatest variations of dosage are associated with Class 2. It would also appear that the distinction between Classes 3 and 4 is not apparent in surface dosage values, but only in the degree of vertical mixing and in the vertical positioning as determined from the vertical dosage profile at WANE.

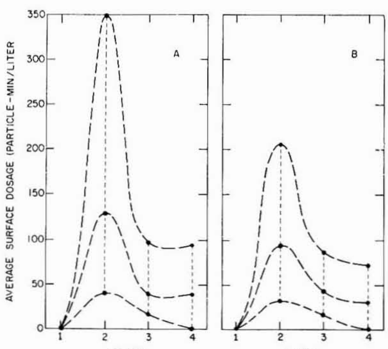

Figure 8. Average and extreme values for each dosage pattern class. A, rural area average dosage; B, city area average dosage

Finally, a most significant feature was the frequency with which the tracer cloud axis was transported downward to ground level. Within the range 1.6 to 12.9 km from the release line covered by the observations, no less than 21 of the 39 cases exhibited this feature. Prior to the conduct of these experiments, it was anticipated that a mesoscale wave pattern in the vertical could be generated by the heat island effect of the city, but it was not expected that this would be of sufficient magnitude and depth to so profoundly alter the trajectory of the cloud.

With these descriptive materials at hand, a generalized version of the now-classic (Gaussian plume) diffusion formula was constructed as follows:

The Gaussian distribution model for the vertical dimension was adopted with important modifications of the meaning of the parameters depending on class of diffusion category under consideration.

The height of the tracer axis was introduced as an exponential function of the distance from the source line.

The second consideration is incorporated by the trajectory equation,

$$z_{\max} = z_0 \exp - \lambda(x - x_0) \tag{1}$$

where $z_{\max}$ is the height of the axis of the cloud at distance x downwind from the release distance; x_0 and z_0 are the height of the cloud release; λ is the single variable parameter in this trajectory term and is to be evaluated from the data. Equation 2 was used to calculate the average vertical velocity of the cloud axis inferred by Equation 1.

$$z_{\max} = z_0 - \frac{w(x - x_0)}{u} \tag{2}$$

The mathematical diffusion model for the surface dosage for $z = 0$ (ground-level concentration) may be written

$$D(x - x_0, 0) = \frac{2Q}{\sqrt{2\pi}\,\bar{u}\sigma_z(x - x_0)} \exp - \frac{1}{2}\left[\frac{z_0^2 e^{-2\lambda(x-x_0)}}{\sigma_z^2(x - x_0)}\right] \tag{3}$$

where D is the average surface dosage at distance $(x - x_0)$ from the release line; Q is the source strength in particles per meter; $\bar{u}$ is the horizontal wind speed evaluated at source height; σ_z is the standard deviation or mixing depth of the vertical dosage distribution and is a function of the distance x from the release line x_0; z_0 is the source height; x_0 is the source line position; and λ is the vertical trajectory coefficient defined in Equation 1. It should be emphasized that Equation 3 was written for and fitted to only the surface dosage pattern. Variable, λ, u, and σ_z were expected to be functions of the meteorological parameters and the source line location. Values were determined from the dependent experimental data cases and predictors were sought from the meteorological measurements. It was determined that σ_z could be fitted as a linear function of distance as shown in Equation 4.

$$\sigma_z(x - x_0) = \sigma_{z_0} + a(x - x_0) \tag{4}$$

The value of σ_{z0} is a measure of the apparent vertical width of the line source created by the dispensing technique.

The fitting procedure led to the specification of the parameters which reproduce the surface dosage patterns in conjunction with Equation 3 within a factor of 2 at each distance for the dependent data group. The fitted parameters are λ, the trajectory parameter; σ_{z_0}, the apparent initial value of

σ_z; and a, the growth rate of σ_z. The source strength Q was computed for each release and the wind speed $\bar{u}$ was that observed at the WANE tower for the appropriate altitude of release.

The lack of vertical profiles of dosage over the rural area and the appearance of the mesoscale circulation pattern which brought the tracer to the ground precluded definitive comparison of the vertical growth rates of the tracer clouds over the rural and urban areas. It was clear from the classification of the surface dosage patterns in the two areas that the city produced more uniform mixing of the cloud.

In an attempt to analyze the change in the vertical growth rate occasioned by the presence of the city and its effects, the following analysis was performed.

According to Taylor's (1921) equation,

$$\sigma_z{}^2 = \overline{2w^2} \int_0^T \int_0^t R(\xi) d\xi dt \qquad (5)$$

where $\sigma_z{}^2$ is the variance of the vertical distribution of the tracer, $\overline{w^2}$ is the intensity of the vertical component of turbulence, $R(\xi)$ is the Lagrangian correlation function for the vertical component of turbulence, and T is the travel time. If we adopt Equation 5 and assume the Lagrangian correlation coefficient, $R(\xi)$, had gone to zero by the time the cloud passes WANE,

$$\sigma_z{}^2(\text{WANE}) = \overline{2w^2}[A(t)T] \qquad (6)$$

where $A(t) = \int_0^\infty R(\xi)d\xi$ is the so-called scale length of turbulence. Taking $T = [X(\text{WANE}) - X_0]/\bar{u}$,

$$\sigma_z{}^2(\text{WANE}) = \frac{2w^2A(t)}{u}[X(\text{WANE}) - x_0] \qquad (7)$$

where $\bar{u}$ is the average horizontal speed of the cloud between the release line and WANE.

Estimates of $\sigma_z{}^2(\text{WANE})$ were made as indicated previously, and $\overline{w^2}$, $\bar{u}$, and $(x - x_0)$ could be measured from the experimental data. From these data, $A(t)$ was estimated for Classes 1–3.

Differentiating Equation 6 with respect to travel time yields

$$\frac{d\sigma_z{}^2}{dt} = \overline{2w^2}A(t) \qquad (8)$$

provided that t is greater than the time required for $R(\xi) \rightarrow 0$: Then

$$\frac{d\sigma_z{}^2}{dx} = \frac{\overline{2w^2}}{\bar{u}} A(t) \qquad (9)$$

From the separate estimate produced previously of $d\hat{\sigma}_z/dx = a$ and Equation 4, we have

$$\frac{d\hat{\sigma}_z{}^2}{dx} = 2a\hat{\sigma}_z \qquad (10)$$

Equation 10 provides the best-fit estimate for the observed rate of change of $\sigma_z{}^2$ with distance over the city. The ratio of Equations 9 and 10 provides a first approximation to the effect of the city in changing the vertical growth rate of the cloud from its expected growth rate over rural areas. If this ratio is defined as R,

$$R = \frac{\overline{w^2}A(t)}{\bar{u}a\sigma_z} \qquad (11)$$

provides the estimate we seek. Average values of R were 0.43 in Class 1, 2.2 in Class 2, and 1.8 in Class 3. In the mean for each diffusion group (other than Class 1) the city increases $d\sigma_z{}^2/dx$ by about 50%. On this basis, the concentration or dosage reduction rate should be increased also by a factor equal to about $\sqrt{2}$, or 1.4. This is a reasonable and probably useful result and is of the right order of magnitude according to the comparative total dosages in the rural and city areas.

In some cases, the growth rate of the cloud appears to be inhibited by the city—*i.e.*, $R < 1$. This can be attributed to the presence of a restricted mixing layer over the city which, by limiting vertical exchange, suppresses the growth of the tracer cloud.

Because of the importance of vertical atmospheric structure and diffusion, primary attention was focused on the study of the predictive value of vertical profiles of wind and temperature values representative of rural conditions. Measurements of the intensity of turbulence, rural and urban surface temperatures and air temperatures, and the vertical profiles of wind and temperature within the city were also available.

Attention was turned to those meteorological quantities which theory and previous measurements indicated should be most closely related to the diffusion parameters, σ_{Z0}, a, and λ.

λ is, of course, a mesoscale parameter which controls the vertical position of the tracer cloud axis as it moves into and through the city, and may depend upon the magnitude of the larger-scale vertical motions induced by the city heat island effect. According to theory, these motions should depend upon the vertical heat flux difference between the city and the rural area and upon the hydrostatic stability of the rural atmosphere. Since the surface air temperature difference between rural and city areas was sensibly constant (and the air temperature differences were) about 4°C during the trial period, no significant prediction of variability could be tested. However, the rural lapse rate varied considerably among these trials, and this quantity was found to be extremely important in predicting the value of λ. This dependence is summarized in Figure 9. When this lapse rate is greater than isothermal,

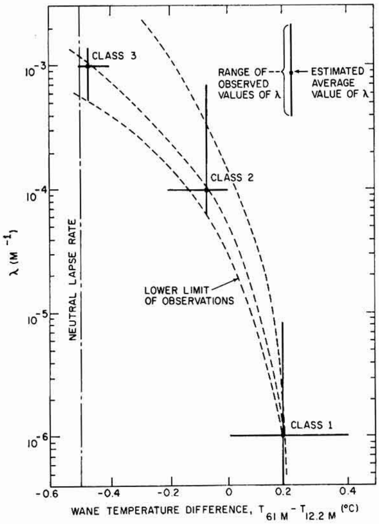

Figure 9. Average and range of values of the vertical trajectory coefficient, λ, as a function of diffusion class and temperature lapse rate observed at WANE-TV tower

the descent is very slow. When the temperature lapse rate goes from isothermal to neutral, the value of λ rises precipitately, indicating an increasing rate and magnitude of the displacement of the cloud axis. When the rural temperature lapse rate is less than adiabatic, general vertical mixing appears to wipe out the effect. This dependence of the cloud centroid on lapse rate is further confirmed by the magnitude of the effect over the rural area, as measured by the average downward velocity of the tracer cloud axis (Figure 10).

While the specification of λ dictates the vertical position of the tracer cloud axis as it passes into and over the target area, z_0 and a determine the vertical distribution of the tracer material, centered about the cloud axis. These two parameters are, therefore, most closely related to the small-scale vertical turbulence intensity and structure.

A comparison of the values of σ_{z0}, λ, and a with the stability as measured at WANE is shown in Figure 11; it is evident that there is a dependence of these diffusion parameters on thermal stability. In fact, numerous attempts to correlate these diffusion parameters with other meteorological measurements failed to reveal any significant relationships. Further analytic attempts to find within-group dependencies of the diffusion parameters on stability also failed.

These dependencies of the transport and diffusion parameters on the temperature lapse rate at WANE are synthesized from the experimental data by comparison of the observed averages and ranges of the average city surface dosage with the WANE observed temperature lapse rate. This comparison is summarized in Figure 12. It is clear from this figure that, while there is overlap of total dosage between diffusion classes, there is a marked dependence of dosage on the rural temperature lapse rate. As should be expected from the mathematical model, which also synthesizes these data, the most sensitive (and therefore most difficult to predict) cases are in Class 2, where the combined effects of slower descent of the cloud axis and slower vertical diffusion rates produce large gradients of tracer concentration in the vertical dimension near the surface.

On the basis of the foregoing analyses, the urban diffusion prediction system is generalized by Equation 3 and the input

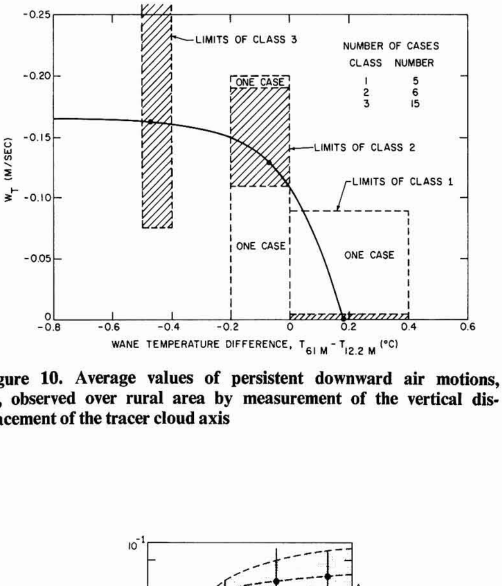

Figure 10. Average values of persistent downward air motions, $\bar{w}_t$, observed over rural area by measurement of the vertical displacement of the tracer cloud axis

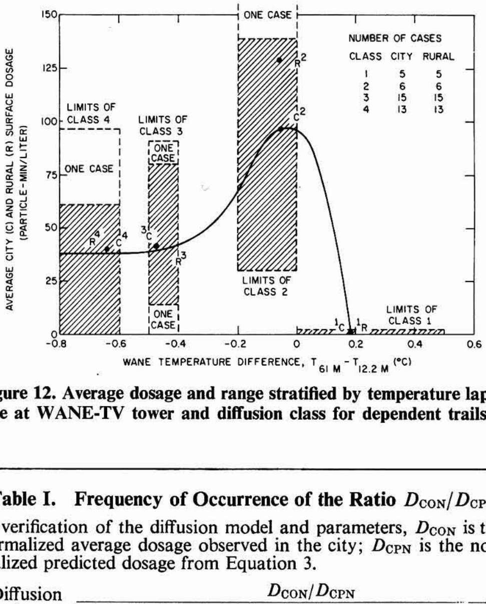

Figure 12. Average dosage and range stratified by temperature lapse rate at WANE-TV tower and diffusion class for dependent trails

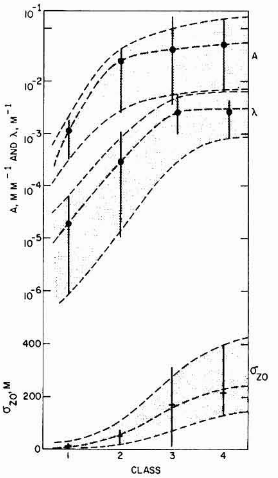

Figure 11. Average and range of the diffusion parameters by diffusion class

Table I. Frequency of Occurrence of the Ratio D_{CON}/D_{CPN}

In verification of the diffusion model and parameters, D_{CON} is the normalized average dosage observed in the city; D_{CPN} is the normalized predicted dosage from Equation 3.

Diffusion class		D_{CON}/D_{CPN}				
	Trials	0.0–0.3	0.4–1.0	1.1–2.0	2.1–3.0	>3.0
1	Ind	. . .	1	. . .	. . .	1
	Dep	. . .	5	. . .	. . .	. . .
2	Ind	. . .	4	1	2	. . .
	Dep	. . .	2	2	1	. . .
3	Ind	. . .	. . .	3	. . .	2
	Dep	. . .	4	8	2	1
4	Ind	1	2	. . .	1	. . .
	Dep	. . .	3	4	4	. . .
All	Ind	1	7	4	3	3
	Dep	. . .	14	14	7	1
Total		1	21	18	10	4

Predicted average dosage:

1. Within a factor of two of the observed dosage:
   72% of the time for all trials
   78% of the time for dependent trials
   61% of the time for independent trials
2. Within a factor of three of the observed dosage:
   90% of the time for all trials
   97% of the time for dependent trials
   78% of the time for independent trials

parameters shown in Figure 11. To verify this prediction system, the experimental surface-dosage values were normalized to a release wind speed of 5 m/sec and a release rate (source strength) of 10^{10} particles/m. Equation 3 was programmed for computer solution with $\bar{u} = 5$ m/sec and $Q = 10^{10}$ particles/m. The output was the average dosage at each of the surface sampling line distances.

The trial-by-trial comparison of predicted *vs.* observed surface dosage patterns was summarized for all valid trials (dependent and independent). Taking the ratio of the observed (normalized) average surface dosage to the predicted surface dosage as the primary measure of the validity of the prediction system, the frequency of success and failure can be summarized as shown in Table I.

With these results, we may conclude that the prediction equation and parameters developed here will provide a specification of the magnitude and mode of surface exposure, in the city, to aerosols released upwind along an elevated line source that is correct to within a factor of 2 about 70% of the time. The only input data required are: the release position (within about 4800 m of the city and below 250 m altitude); the source strength, Q, in particles/m; the wind speed at release height, $\bar{u}$, in m/sec; and the stability in the lower 61 m of the rural atmosphere.

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Oxidation of *n*-Butane by the Photolysis of NO_2

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■ The photooxidation of *n*-butane was investigated in the presence of nitrogen oxides and ultraviolet light. Although the amount of *n*-butane reacted is low, its presence facilitates the oxidation of nitric oxide. The presence of carbon monoxide increases the rate of oxidation of nitric oxide. Mechanisms for the photooxidation of *n*-butane and the role of carbon monoxide in the oxidation of nitric oxide are discussed. Hydroxyl radicals are postulated as the principal chain-propagating free radicals. Products such as ozone, peroxyacetyl nitrate, carbon monoxide, carbon dioxide, methyl ethyl ketone, and aldehydes are observed.

Laboratory studies related to photochemical air pollution are generally concentrated on the photodissociation of nitrogen dioxide in the presence of olefins or aromatics. Such systems are chosen because olefins and aromatics react quickly, and the usual products such as aldehydes, oxidant, and PAN are observed. The lower-molecular-weight saturated hydrocarbons have been largely ignored because their reactivity is very low, even with prolonged irradiations. Altshuller and coworkers (1969a) recently showed, however, that the photooxidation of *n*-butane at low nitrogen oxide levels can yield significant quantities of oxidant. Oxidant forms even though very little hydrocarbon has reacted. This observation is important in air pollution research since ozone production is one measure by which hydrocarbons are characterized in reactivity scales (Altshuller, 1966).

The work described here was undertaken to study the oxidation of *n*-butane in the presence of light and nitric oxide. We attempted to extend the work of Altshuller and coworkers and to elucidate the mechanism by which *n*-butane reacts.

Experimental

The irradiations were carried out in three chambers: a 335-ft^3 chamber described earlier (Korth *et al.*, 1964), a floor-type irradiation chamber containing a 150-liter Teflon FEP bag (Altshuller and Cohen, 1964), and a 22-liter flask containing an immersion well, equipped with a Hanovia mercury arc.

Gas samples drawn from the 335-ft^3 chamber and the 22-liter flask for analysis were replaced with purified air and 20% oxygen in helium, respectively. The quantities of gases added were measured to correct the chamber analysis for dilution of the reaction mixture. No corrections were needed for the 150-liter bag since the sample was not diluted by sampling.

Analyses were done with gas chromatographs; an SF-96 column was used for the *n*-butane analysis, a Polypak 1 for water, a Porapak Q for CO_2, a silica gel for CO and CO_2, and a Teflon-walled Carbowax 1540 column for methyl ethyl ketone, acetaldehyde, PAN, and methyl nitrate. PAN and methyl nitrate were analyzed with an electron-capture detector. Water was analyzed on a Beckman GC-5 gas chromatograph equipped with a helium photoionization detector. Bureau of Mines helium was used with this detector. All other compounds were analyzed with the flame ionization-type detector. CO and CO_2 were hydrogenated over a nickel catalyst before being analyzed on a flame-ionization detector. Nitrogen dioxide was measured by the conventional colorimetric procedure. Oxidant was measured by the Mast ozone analyzer.

The first-order dissociation constant for NO_2, k_d, was obtained by photodissociation of nitrogen dioxide in the ppm range (v/v) in nitrogen (Tuesday, 1961). The equation used for this was $d(NO_2)/dt = k_d(NO_2)$. Since $k_d = 1.5\ k_a\phi$, this first-order dissociation constant is a measure of the light intensity. The k_d values were 0.40 min^{-1} for the 335-ft^3 chamber, 0.36 min^{-1} for the 150-liter plastic bag reactor, and 1.29 min^{-1} for the 22-liter reactor. The temperatures for the three chambers were, 31 °C ± 1 ° for the 335-ft^3 chamber, 25 °C ± 1.5 ° for the 150-liter chamber, and 28 °C at equilibrium for the 22-liter chamber. The immersion well containing the Hanovia mercury arc was cooled with refrigerated water.

Results and Discussion

Figures 1 and 2 present data obtained from the photooxidation of *n*-butane in the 335-ft^3 chamber. Figure 1 shows that the hydrocarbon reacts linearly with irradiation time. This linearity apparently is independent of light intensity, since the same phenomenon was observed with the 150-liter reactor and with the 22-liter chamber with the very high light intensity (k_d = 1.29 min^{-1}). The linearity is lost only after prolonged irradiation (Figure 3). The observed rate of reaction of *n*-butane is compared in Table I to the calculated rate of O-atom reaction with *n*-butane for irradiations in the 150-liter and 335-ft^3 chambers. The calculated rate was obtained by using the rate of reaction between atomic oxygen and *n*-butane. The steady-state concentration for atomic oxygen was calculated with the equation derived by Ford and Endow (1957). The rate constant used for the calculation was 2.5 × 10^7 liter/mol sec (Elias and Schiff, 1960). The *n*-butane–ozone reaction, which is too slow to be of importance in this system, was not considered in the calculated rate of reaction of *n*-butane.

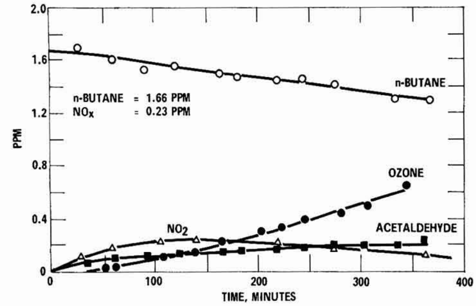

Figure 1. Photooxidation of *n*-butane in the presence of oxides of nitrogen

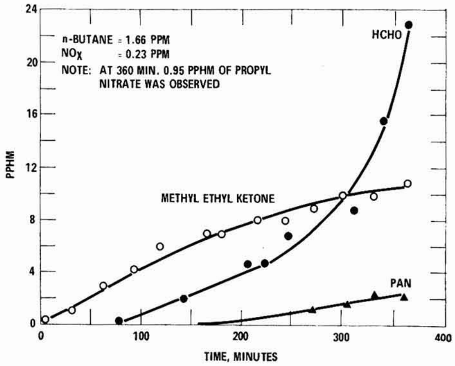

Figure 2. Product formation from photooxidation of *n*-butane

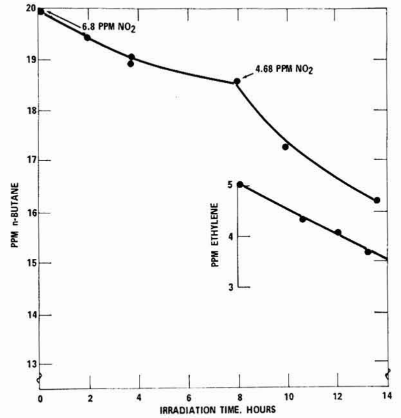

Figure 3. Change in rate of reaction of *n*-butane with the addition of ethylene

The last column in Table I shows the ratio of observed to calculated rates. Except for very low hydrocarbon concentrations, the ratio is very large. This indicates that the reaction of atomic oxygen and *n*-butane acts only as an initiating reaction. Most of the hydrocarbon is consumed by other reactive species. In this respect, *n*-butane acts very much like the aromatics, with which most of the hydrocarbon consumption is attributable to free-radical species (Altshuller and Bufalini, 1965). If the atomic oxygen reaction were the most important reaction, the slope (column 4) should be directly dependent upon the nitrogen dioxide concentration shown in column 2. The data do not show any such correlation.

Since atomic oxygen–*n*-butane reaction acts only as a chain-initiating reaction, a mechanism must be written to explain the large differences between the observed and calculated rates. The suggested mechanism is similar to that proposed by Fish (1968) in the absence of nitric oxide.

$$NO_2 + h\nu \rightarrow NO + O \qquad (1)$$

$$O + O_2 \xrightarrow{M} O_3 \qquad (2)$$

$$C_4H_{10} + O \rightarrow C_4H_9 + OH \qquad (3)$$

$$C_4H_9 + O_2 \rightarrow C_4H_9O_2 \qquad (4)$$

$$C_4H_9O_2 \rightarrow \text{epoxybutane} + OH \qquad (5a)$$

$$\rightarrow \text{methyl ethyl ketone} + OH \qquad (5b)$$

$$\rightarrow CH_3CHO + C_2H_5O \qquad (5c)$$

$$C_4H_{10} + OH \rightarrow C_4H_9 + H_2O \qquad (6)$$

Table I. Observed and Calculated Rates for Photooxidation of *n*-Butane

n-Butane, ppm	NO_2, ppm	Rel. humidity, %	Obs. rate, ppm/min × 10^3	Calcd rate,[a] ppm/min × 10^5	Obs. to calcd ratio
12.0	0.45	5	2.2	2.90	76
9.00	0.50	5	0.52	2.18	24
6.18	0.35	32	1.8	1.15	160
3.03	0.19	32	1.7	0.300	570
2.85	0.14	5	0.92	0.195	470
2.75	0.57	50	0.43	0.758	57
2.30	0.42	50	0.45	0.468	96
1.35	0.33	32	0.70	0.230	300
0.77	0.56	5	0	0.213	0

[a] Calculated rate based on O-atom reaction with *n*-butane.

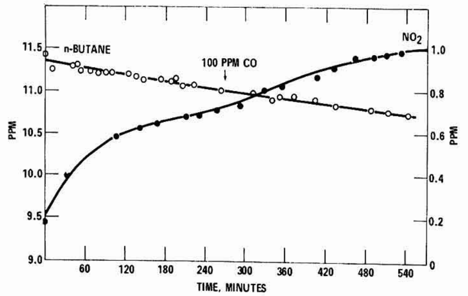

Figure 4. Effect of added carbon monoxide on the rate of oxidation of nitric oxide

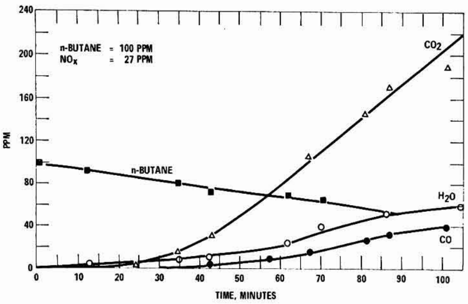

Figure 5. Photooxidation of *n*-butane at high light intensity

This mechanism makes hydroxyl radicals the principal chain-propagating free radicals. Since rate constants between OH and hydrocarbons are quite large (Greiner, 1967), the disappearance of *n*-butane can be easily explained. To test the importance of hydroxyl radicals in this mechanism, CO was added at the time indicated in Figure 4. Several replicate runs were performed in this manner and, in each case, the nitrogen dioxide formation rate increased. In some cases, the rate of disappearance for *n*-butane also increased, but the reproducibility was poor.

The increase in nitric oxide oxidation can be explained by Reactions 7–9, as recently discussed by Heicklen (1969).

$$OH + CO \rightarrow CO_2 + H \qquad (7)$$

$$H + O_2 \rightarrow HO_2 \qquad (8)$$

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (9)$$

The products that were observed are shown in Figures 1, 2, and 5.

Epoxybutane (Reaction 5a) was included as a product, but it is doubtful that this reaction is important unless the epoxide is tetrahydrofuran. All other epoxybutanes had gas chromatographic retention times incompatible with those observed. Tetrahydrofuran was unavailable and was not tested.

Methyl ethyl ketone appears early in the reaction and can be explained by Reactions 5b, 10, and 11.

$$C_4H_9O_2 + NO \rightarrow C_4H_9O + NO_2 \qquad (10)$$

$$C_4H_9O + O_2 \rightarrow C_4H_8O + HO_2 \qquad (11)$$

Acetaldehyde is also formed early in the reaction. Its formation can be explained by Reaction 5c. Although Reaction 12 could also explain its formation, ethylene has not been observed as a product.

$$C_4H_9O_2 \rightarrow OH + CH_2 = CH_2 + CH_3CHO \qquad (12)$$

Reaction 13 is also apparently unimportant in the formation of acetaldehyde (East and Phillips, 1967).

$$C_4H_9O \rightarrow CH_3CHO + C_2H_5 \qquad (13)$$

Since no hydroperoxides have been observed as products, Reactions 14 and 15 can be eliminated.

$$C_4H_9O_2 + C_4H_{10} \rightarrow C_4H_9O_2H + C_4H_9 \qquad (14)$$

$$C_4H_9O_2 + CH_3CHO \rightarrow C_4H_9O_2H + CH_3CO \qquad (15)$$

Reaction 14 apparently can be eliminated from bond energy considerations, but it is difficult to understand why Reaction 15 does not occur. *R*O$_2$ radicals must either decompose rapidly via Reaction 5 or undergo rapid reaction with nitric oxide (Reaction 10).

Carbon dioxide and carbon monoxide appear late in the reaction with the high light intensity source, as shown in Figure 5. These products must result in the photooxidation of secondary products since most of the carbon can be accounted for as CO and CO$_2$. Other products that have been qualitatively observed but are not shown in the figures are methyl nitrate, ethyl and isopropyl nitrate, diacetyl, *tert*-butyl nitrate, ethanol, acetone, and formaldehyde. Once formed by Reaction 2, ozone apparently is undisturbed by the system, since its reactivity with saturated hydrocarbons is very low. This is why large quantities of ozone are observed in the photooxidation of *n*-butane (Altshuller *et al.*, 1969a). The formation of PAN can be explained by Reactions 16 to 19.

$$CH_3CHO + O \rightarrow CH_3CO + OH \qquad (16)$$

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \qquad (17)$$

$$CH_3CO + O_2 \rightarrow CH_3CO_3 \qquad (18)$$

$$CH_3CO_3 + NO_2 \rightarrow CH_3CO_3NO_2\ (\text{PAN}) \qquad (19)$$

Several experiments were performed to note the effect of added ethylene on the photooxidation of *n*-butane. These data are shown in Figure 3. The presence of ethylene greatly accelerates the rate of reaction of *n*-butane. These observations may be contrasted with some earlier findings of Altshuller *et al.* (1969b), who found no difference in the reaction rate of *n*-butane when propylene and toluene were added. However, the comparison may not be valid since these investigators used much lower concentrations (3 ppm of *n*-butane and 0.25 to 0.5 ppm of propylene) and a much lower light intensity (k_d of 0.36 min^{-1} *vs.* 1.29 min^{-1}). In addition, the starting NO$_x$ mixture was mostly NO not NO$_2$. These factors may contribute to accounting for the differences in addition to the use of a different olefin. Assuming that both observations are correct, we must conclude that the free radicals produced by the photooxidation of ethylene are not the same as those produced by the photooxidation of propylene and toluene. Although further work is needed to clarify this point, these findings strongly suggest that hydroxyl radicals are also produced in the photooxidation of ethylene–NO$_x$ systems.

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A Simple, Rapid Method for Determining Trace Mercury in Fish via Neutron Activation Analysis

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■ A simple, rapid neutron activation method for mercury in fish tissue is described. The technique employs separation of the activated mercury as an $HgCl_4^{2-}$ complex on an anion-exchange resin and direct counting of the resulting resin. Results showed that the analyses have a $\pm 10\%$ standard deviation for tissue samples containing mercury in the 0.05 to 10 ppm range, and the sensitivity has an approximate 3-ppb limit for the conditions employed. Example results for mercury content in different fish species from a variety of locations and different fish organs are given. Also, the results of replicate samples analyzed by a variety of different methods and in different laboratories are compared.

As a consequence of the recent concern over mercury pollution in the environment, the development of simple, rapid analytical methods for the accurate determination of trace amounts of mercury has become very important. It is especially important that such a method be accurate and reproducible as the principal problem in environmental and pollution studies is that of getting reliable analytical data. This paper describes the application and results of a modified version of a neutron activation analysis (NAA) (Bowen and Gibbons, 1963) which has been conveniently used for determining mercury in fish tissue.

The method of Bowen and Gibbons (1963), based on a technique originated by Ehman and Huizinga (1959), employs (after irradiation, dissolution of the sample, and dilution with HCl) an anion-exchanging column on which the mercury, as a $HgCl_4^{2-}$ complex, is absorbed. Other interfering cations, $^{24}Na^+$ in particular, are not absorbed and pass through the column. In the Bowen and Gibbons (1963) method, the $HgCl_4^{2-}$ complex is subsequently eluted with HNO_3 and then precipitated as HgS from solution for counting. We found quantitative and (or) reproducible elution of the mercury from the exchange resin difficult, as well as requiring large amounts of the HNO_3 solution for optimum results. Thus, the method was modified to count the exchange resin directly, thereby eliminating the subsequent chemical steps which seemed to result in losses and (or) irreproducibility. It is also shown that the standard radiochemical technique of adding a holdback carrier prevents large losses of the sample mercury during the digestion and the chemical steps preceding the ion-exchange step and, thus, has great advantage over other techniques that do not use NAA for the determination.

Weighed fish tissue samples of 0.8 to 1.0 g are individually sealed in quartz tubes (4 in. × 0.25 in.). Also from the same specimen, tissue plus an exactly known amount of $HgNO_3$ as an internal standard are individually sealed in individual quartz tubes. The quartz ampoules containing both the unknown and internal standard are then irradiated together in the Ford Nuclear Reactor of the Michigan Memorial-Phoenix Project (neutron flux of 10^{13} neutrons/cm^2/sec) for 36 hr. After a delay of two to three days, to allow the gross activity to decay to a level where the samples can be safely handled, each ampoule is broken open after freezing in liquid N_2, the contents placed in a 125-ml Erlenmeyer flask, and 1.0 ml of the mercury holdback carrier (20 mg Hg^{2+}/ml) added.

The samples are then covered with a watch glass and digested with just sufficient 1:1 concentrated $HNO_3:H_2SO_4$ to bring the samples into solution. (This typically requires about 5 ml of the acid mixture.) After cooling, the solutions are diluted to 25 ml with $1M$ HCl. This solution is then passed at a flow rate of about 5 ml/min through an ion-exchange column

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[1] Present address: BASF-Wyandotte Chemicals Corp., Wyandotte, Mich. 48192.

containing 10 cc of Dowex, 2×8 (50 to 100 mesh) ion-exchange resin that has been previously equilibrated with 1*M* HCl. The flask is rinsed several times with 1*M* HCl and the rinsings passed through the column. To remove all the $^{24}Na^+$ from the column, about 100 ml of the 1*M* HCl in 10-ml aliquots is passed through the column. The resin is then removed from the column, placed in a glass vial, and counted for 400 sec by a Canberra 25 cc coaxial Ge (Li) detector and a Nuclear Data 4096 channel analyzer. The area under the 77.3 KeV gamma photopeak of ^{197}Hg ($t_{1/2}$ = 65 hr) is used to determine the amount of mercury present in the sample and internal standard. The additional activity present in the internal standard over that in the sample is used to calculate the activity per μg of mercury present, and this is used to calculate the amount of mercury originally present in the sample.

Experiments were also carried out to determine if it was necessary to use a replicate fish tissue sample in the tube employed as a reference Hg standard in the procedure. If not, the time needed for preparation of the tissue sample for irradiation could be shortened, as the standards could be prepared in quantity in advance. These standards were prepared by pipetting 100 λ aliquots of standard mercury solution (10 μg Hg^{2+}/ml) into individual quartz ampoules and sealing them. One standard ampoule and two samples were then tied together with aluminum wire for irradiation. The standard received the same chemical treatment as the samples. Extensive comparisons between "external" and "internal" standard tests showed no significant difference in the amounts of mercury found and it appears that either method can be used with success. Note, however, that in both cases, the amount of standard mercury should be of the same order of magnitude as that expected in the samples, so that dead time losses in the analyzer are comparable. Also, unsuspected interferences (not present in any sample tested here) might lead to error when "internal" standards are not used.

Fish samples supplied by the U.S. Bureau of Commercial Fisheries, Ann Arbor, Mich., and others obtained independently were analyzed directly. As the amounts of mercury actually present in the samples were unknown, comparisons were made between our results and those obtained by other laboratories with use of various methods such as atomic absorption, NAA, and x-ray fluorescence. Table I shows a comparison of analytical results obtained for the same fish tissue samples.

Results and Discussion

In all cases, the results compared favorably for the same samples, and replicate results using the method described showed less scatter than those reported by the other laboratories. It should be pointed out that the fish tissue showed very large inhomogeneity of Hg content. Thus, all samples were ground and mixed carefully before analysis. The mercury content reported represents total concentration in the whole tissue sample as provided.

As a further test, a whole Coho salmon, caught in Lake Erie, was obtained from the U.S. Bureau of Commercial Fisheries for the purpose of comparing mercury content in various organs with that in the edible tissue. The results are shown in Table II. It is interesting to note that the Hg concentration varies significantly in the various organs of the fish. Further study of the Hg distribution in fish is in progress.

In an attempt to obtain Hg-free tissue samples (zero Hg content fish tissues) for use as a "zero" blank in the determination, fish from several bodies of water remote from known sources of Hg pollution were tested. All samples showed significant amounts of mercury (Table III) and samples containing "no mercury" were not obtainable.

As a result of numerous analyses, the lower limit of detection is estimated to be 3 ppb ± 20%, based on counting statistics. This limit could easily be lowered by use of a higher neutron flux, longer irradiation time, and (or) longer counting time. In the concentration range of mercury found in fish tissue, 0.05 to 10 ppm, the standard deviation of results was ±10%.

Bromide ion in the sample was the only potential interference in this method. The bromide ion is retained on the ion-

Table I. Representative Results of Hg Analyses in Edible Fish Tissue

Method	Results, ppm
Sample 1	
Atomic absorption[a]	0.60[b]
Atomic absorption[a]	1.0[b]
Atomic absorption[a]	0.85[b]
X-ray fluorescence	0.40[b]
Destructive NAA	0.87[b]
This method	0.86 (10% SD)
Sample 2	
This method	0.58 (10% SD)
NBS (nondes. NAA)[c]	0.54
Average results of 15 labs (various methods)[b]	0.51 (range, 0.19 to 1.2)

[a] Atomic absorption results of three different laboratories.
[b] Results supplied by Grieg (1970).
[c] Results supplied by LaFleur (1970).

Table II. Hg Content in Various Fish Organs and Tissue

Sample source	Hg found, ppm
Edible tissue	0.48
Brain	0.23
Stomach	0.17
Kidney	0.36
Liver	0.87
Heart	0.44

Table III. Hg Content in Fish from Various Geographical Locations

Type of fish	Source	Hg found, ppm
Large mouth bass	Bonham State Park Lake, Tex.	0.14
White fish	Northern Lake Huron	0.05 to 0.15[a]
Blue gill	Sandy Bottom Lake, Mich.	0.40
Rock bass	Sandy Bottom Lake, Mich.	0.42
Coho salmon	S.W. Lake Erie	0.48
White bass	Western Lake Erie	0.60
Yellow perch	Western Lake Erie	0.17
Yellow perch	Eastern Lake Erie	0.34
Walleyed pike	Lake St. Clair, Mich.	1.56

[a] Several different fish.

exchange resin and the ^{82}Br ($t_{1/2}$ = 26 hr) spectrum is a major component of the total gamma spectrum of the sample (Figure 1). However, with the high resolution of the Ge (Li) detector, concentrations of bromide ion in the levels found in the many samples examined could be easily tolerated without causing any measurable error in Hg determination. No interference was found for any other metal ion in the fish tissue studied. Furthermore, with the volume of 1*M* HCl used in the rinse and sodium elution, no detectable mercury (as a loss) was found in these solutions after passing through the column, and only trace amounts of $^{24}Na^+$ remained on the column.

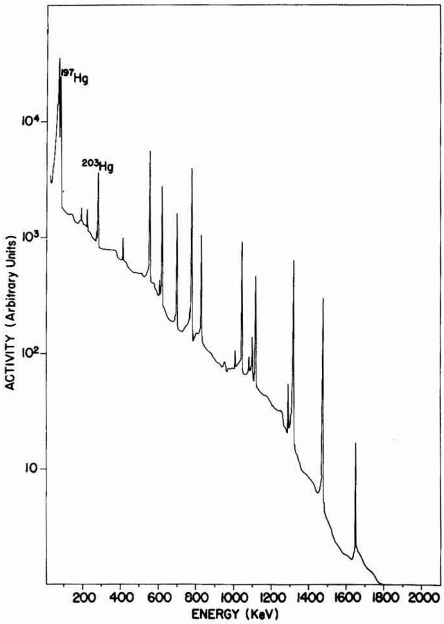

Figure 1. The gamma spectrum of the ion-exchange resin containing Hg sample

This technique has advantages over other methods of trace-Hg analysis. Especially with the addition of "carrier" mercury after irradiation, the percent losses of sample mercury during chemical separation are lowered significantly compared to other methods. Elimination of chemical steps in the Bowen and Gibbons (1963) method shortens the analysis time per sample. In addition, several samples can be run simultaneously by one technician so that the total time for preparation and counting of each unknown can be lowered to about 10 to 15 min per sample.

Acknowledgment

This work was supported by the Michigan Memorial Phoenix Project, which also donated laboratory space and reactor time, NSF grant GA-25563, and the Federal Water Quality Administration grant no. 16020-ELH. Also, we thank Richard Grieg, U.S. Bureau of Commercial Fisheries, who supplied fish samples and the comparative data.

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Tritium Loss from Water Exposed to the Atmosphere

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■ Equations describing the loss of HTO from water into air and the gain of HTO in water when the overlying water vapor contains tritium but the solution does not are developed and verified by laboratory experiments. Results show that under environmental conditions, where the relative humidity is greater than 8%, HTO is lost preferentially over H_2O to the atmosphere because atmospheric moisture is virtually free of HTO. Results from a three-year study of the changes in tritium content of a large nonseeping outdoor basin are used to extend the laboratory studies to field situations. Data from this field study were used to calculate tritium loss from open basins. These calculations show, for example, that 90% of the tritium contained in an aqueous stream flowing at 15,000 liters per day will be lost to the atmosphere from a shallow basin with a surface area of 6000 m.^{2}

Small quantities of tritium as HTO are found in much of the process water that is used in certain nuclear facilities. This tritium, usually a by-product of the fission of uranium, gets into the aqueous streams as a result of chemical processing (Albenesius and Ondrejcin, 1960). The tritium may also get into other streams as a result of the loss of moderator from heavy water moderated reactors. The heavy water contains tritium from the neutron activation of deuterium (Matic-Vukmirovic *et al.*, 1964). Although there is no feasible way for nuclear facilities to remove and concentrate this small quantity of tritium from the process water, the water is usually released into streams or open basins excavated in the ground. From streams, tritium may be lost to the atmosphere or may flow to the ocean. From open basins, tritium may be lost to the atmosphere or may seep to the groundwater.

Tritium-level changes observed in Savannah River Plant (SRP) waste seepage basins that were exposed to the atmosphere led to a consideration of the theoretical principles involved in the transfer of tritium across an air–water interface. These principles were then demonstrated in laboratory tests and used to explain the concentration changes observed in one of these large basins. These principles are reported so that they may be useful to the management of waste streams that contain tritium.

Theory

The evaporation of water into moist air is a dynamic process in which water molecules continuously evaporate from, and condense on, the surface. The overall rate of evaporation is the difference between the rate at which molecules leave the surface and the rate at which molecules (not necessarily the same ones) condense onto the surface. When tritiated water evaporates into moist air, the rates of the evaporation and condensation processes will be different for H_2O and HTO; both species will leave the surface, but in general, much more H_2O will return because the atmosphere contains very little HTO.

The rate of water evaporation into the atmosphere is usually limited by the diffusion of water vapor through a quiescent layer of air near the surface (Dorsey, 1940). In this model, a stagnant layer of air, which does not mix with the rest of the atmosphere, exists at the surface. The air immediately adjacent to the surface is saturated with water vapor, while that at the other side of the quiescent layer has the same water content as the bulk of the atmosphere. Water vapor is transported by eddy diffusion, molecular diffusion, or both, across this concentration gradient from the surface into the bulk atmosphere. In any case, the steady-state solution of the diffusion equation with these boundary conditions yields the equation

$$m_W = K(P_W - P_W{}^0) \tag{1}$$

where m_W is the number of moles of water transported per unit time and area from the gas phase into the liquid; P_W is the partial pressure of water vapor in the bulk atmosphere; $P_W{}^0$ is the partial pressure of water vapor in the air that would be in equilibrium with the liquid at the same temperature; and K is a parameter that depends on the diffusion coefficient of water vapor in air, the thickness of the quiescent layer, and the temperature. The value of K depends on weather conditions; however, it may be treated as a constant under any fixed set of conditions.

The evaporation of tritiated water must be treated as that of a two-component system. H_2O and HTO will diffuse through the quiescent layer to a first approximation as if the other were not present, because the partial pressure of each is small compared to that of the air. An equation similar to Equation 1 will then be valid for each of the components. The partial pressure of each component in the air at the interface is the equilibrium partial pressure of that component in the liquid phase. Because Raoult's law is obeyed by mixtures of H_2O and HTO (Smith and Fitch, 1963), the equilibrium partial pressure of each component will be equal to the product of vapor pressure of the pure component, $P_i{}^0$, and its mole fraction, N_i, in the liquid mixture. If P_i is the partial pressure of a component in the atmosphere at the other side of the stagnant layer, the rate of transport would be

$$m_i = K(P_i - P_i{}^0 N_i) \tag{2}$$

where i refers to either component. Subscripts T and W in the following equations refer to quantities related to HTO and H_2O, respectively. Constant K is assumed to be the same for both species because the thickness of the quiescent layer is the same and the diffusion coefficients are nearly the same.

In typical environmental conditions, the amount of HTO present will be very small compared with that of H_2O. The mole fraction of H_2O will then be one for all practical purposes, and Equation 2 will become identical to Equation 1 for H_2O.

The mole fraction of HTO, similarly, can be replaced by the mole ratio of HTO to H_2O, n_T/n_W, and Equation 2 can be expressed as

$$\frac{dn_T}{dt} = K\left(P_T - P_T{}^0 \frac{n_T}{n_W}\right) \tag{3}$$

where dn_T/dt is the rate of change of moles of tritium in the liquid phase under a unit area of surface, and n_T and n_W are the number of moles of HTO and H_2O in the liquid under the same area. Because $n_T \ll n_W$, n_W can be expressed in terms of the volume per unit area, z (*i.e.*, the depth), the density ρ, and the molecular weight of H_2O, M_W,

$$n_W = \frac{\rho z}{M_W} \tag{4}$$

and n_T can be expressed in terms of z and the concentration of HTO, C, in the liquid.

$$n_T = Cz \tag{5}$$

Differentiation of Equation 5 yields

$$\frac{dn_T}{dt} = C\frac{dz}{dt} + z\frac{dC}{dt} \tag{6}$$

Substitution of Equations 4–6 into Equation 3 yields

$$\frac{dC}{dt} + \frac{C}{z}\left(\frac{dz}{dt} + \frac{KM_W P_T{}^0}{\rho}\right) = \frac{KP_T}{z} \tag{7}$$

Differentiating Equation 4 and substituting into Equation 1, knowing that $dn_W/dt = m_W$, yield

$$\frac{dz}{dt} = \frac{KM_W}{\rho}(P_W - P_W{}^0) \tag{8}$$

Equation 8 represents the change in the depth of a basin as a result of evaporation alone. In real environmental problems, rainfall will also change z. If R is the rate of rainfall, Equation 8 becomes

$$\frac{dz}{dt} = \frac{KM_W}{\rho}(P_W - P_W{}^0) + R \tag{9}$$

Equation 7 is a linear first-order differential equation which can be solved explicitly for C as a function of t if z, $P_T{}^0$, and P_T are known functions of time t. C is assumed to be independent of z, which implies a well-mixed system. A number of interesting special cases can be solved if $P_T{}^0$, P_T, and dz/dt are constant. If we define

$$\frac{dz}{dt} \equiv S \text{ (constant)} \tag{10}$$

$$\frac{KM_W P_T{}^0}{\rho} \equiv \beta \tag{11}$$

$$KP_T \equiv \gamma \tag{12}$$

then

$$z = z_0 + St \tag{13}$$

and Equation 7 becomes

$$\frac{dC}{dt} + \frac{C}{z}(S + \beta) = \frac{\gamma}{z} \tag{14}$$

The general solution of Equation 14 subject to Equation 13 is

$$\frac{C - C_\infty}{C_0 - C_\infty} = \left(1 + \frac{St}{z_0}\right)^{-(1+\beta/S)} = \left(\frac{z}{z_0}\right)^{-(1+\beta/S)} \tag{15}$$

where C_0 is the value of C at $t = 0$ and

$$C_\infty = \frac{\gamma}{S + \beta} \tag{16}$$

It is seen from Equation 14 that C_∞ is the value of C when $dC/dt = 0$, and hence is the steady-state value.

Several special subcases can be derived from Equation 15. If $P_W = P_W{}^0$ in Equation 8 or if the rainfall rate is equal to the evaporation rate in Equation 9, $S = 0$ and Equation 15 (or the general solution of Equation 14) becomes

$$\frac{C - C_\infty}{C_0 - C_\infty} = \exp\left(\frac{-\beta t}{z_0}\right) \tag{17}$$

If no tritium is in the gas, $P_T = 0$, hence $C_\infty = 0$, and Equation 17 becomes

$$\frac{C}{C_0} = \exp\left(\frac{-\beta t}{z_0}\right) \tag{18}$$

If no tritium is initially in the liquid phase, but is in the vapor, $C_0 = 0$ and C_∞ is finite. Equation 17 becomes

$$\frac{C}{C_\infty} = 1 - \exp\left(\frac{-\beta t}{z_0}\right) \tag{19}$$

If tritiated water evaporates into air containing H_2O, but no HTO, and there is no other source of water, such as rain, $S = (KM_W/\rho)(P_W - P_W{}^0)$. Equation 15 becomes

$$\frac{C}{C_0} = \left(\frac{z}{z_0}\right)^{-[1+P_T{}^0/(P_W - P_W{}^0)]} \tag{20}$$

If the air is dry, $P_W = 0$, and

$$\frac{C}{C_0} = \left(\frac{z_0}{z}\right)^{[1-(P_T{}^0/P_W{}^0)]} \tag{21}$$

Because $P_T{}^0/P_W{}^0 = 0.92$ at 25 °C. (Sepall and Mason, 1960)

$$\frac{C}{C_0} = \left(\frac{z_0}{z}\right)^{0.08} \tag{22}$$

Experimental

The derived equations were validated by laboratory experiments that were performed under the conditions described in Table I.

The transfer of HTO across an air–water interface was measured by using stoppered 250-ml. bottles initially containing 100 ml. of liquid (Figure 1). The depth of liquid was 4.6 cm. The space above the liquid was swept with 600 cc. of air per minute. The bottles were weighed daily to determine the volume of water remaining, and, at the same time, 0.1 ml. of liquid was removed for tritium analysis. The tritium was analyzed for by liquid-scintillation counting. Each experiment was replicated four times. The experiments were conducted at 24.5 °C. ± 1°. In these experiments, the samples were hand

Table I. Experimental Conditions for Laboratory Experiments

Experiment	Water content of air above water	Tritium concn of water vapor in air, μCi/ml. of water	Water content of bottle	Initial tritium concn of water, μCi/ml. of water
1	Saturated[a]	0	Remained nearly constant	5
2	Dry[b]	0	Maintained at 100 ml with distilled H_2O	5
3	Saturated[a]	5	Remained nearly constant	0
4	Dry[b]	0	Allowed to decrease	5

[a] The air was saturated by bubbling it through a column of water 90-cm. long and 4-cm. in diameter.

[b] The air was dried by passing it through a column of silica gel 115-cm. long and 6-cm. in diameter, and then through a column of molecular sieve 28-cm. long and 3.5-cm. in diameter.

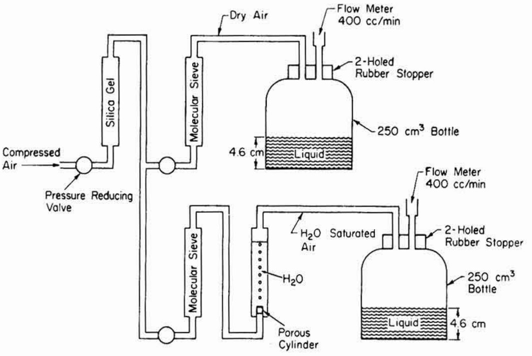

Figure 1. Apparatus used in laboratory experiments

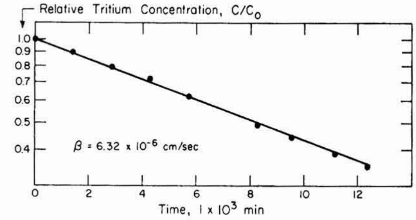

Figure 2. Relative tritium concentration in water when H_2O-saturated air flowed across water surface

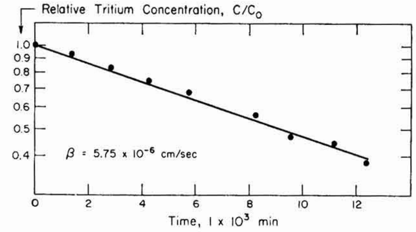

Figure 3. Relative tritium concentration in water when dry air flowed across water surface and the water evaporated was replenished with distilled H_2O

shaken twice a day because preliminary tests showed that mechanical stirring added heat to the system.

Experiment 1 measured the tritium that evaporated from liquid water into air saturated with water vapor. Experiment 2 measured the tritium that evaporated into dry air, but the volume of liquid was kept constant to simulate rainfall. Both experiments represent conditions where $S = 0$ (constant volume), P_T and $C_\infty = 0$ (no HTO in air), and $C_0 \neq 0$, (HTO initially in liquid). Therefore, Experiments 1 and 2 should be described by Equation 18. Figures 2 and 3 are plots of log C/C_0 *vs.* t for Experiments 1 and 2, respectively. The linear behavior in both cases demonstrates that Equation 18 is valid. β, a value proportional to the rate at which the tritium concentration of the liquid changes, was calculated to be 6.32×10^{-6} cm./sec. with a standard deviation of 0.34×10^{-6} cm./sec. for Experiment 1, and 5.75×10^{-6} cm./sec. with a standard deviation of 0.36×10^{-6} cm./sec. for Experiment 2. The slope of the line in each figure equals $-\beta/z_0$. The similarity of the results clearly demonstrates that H_2O and HTO evaporate independently, and that the rate at which HTO is lost from water is not determined by the amount of H_2O vapor in air.

Experiment 3 represents conditions where $S = 0$ (constant volume), $C_0 = 0$ (no HTO initially in liquid), P_T and $C_\infty \neq 0$ (HTO in air). This experiment should therefore be described by Equation 19. A plot of log $[1 - (C/C_\infty)]$ *vs.* t in Figure 4 agrees with the linear behavior expected from Equation 19. β calculated from the slope of that line was 6.00 cm./sec. $\pm$ 0.34×10^{-6}.

Experiment 4 represents conditions where $S = -KM_WP_W{}^0/\rho$ (evaporation into dry air with no replenishment of H_2O), P_T and $C_\infty = 0$ (no HTO in air), and $C_0 \neq 0$ (HTO initially in liquid). The depth of water z should therefore decrease linearly with time (Equation 13 with $S = -KM_WP_W{}^0/\rho$), while the concentration of tritium in liquid should increase with time as described by Equation 22. Figure 5 is the plot of z/z_0 *vs.* t and gives the linear plot expected from Equation 13. The value S calculated from the slope of the line was -5.5×10^{-6} cm./sec. Figure 6 is the plot of C/C_0 *vs.* t and gives the expected increase in tritium concentration in liquid predicted by Equation 22. The solid curve in Figure 6 is the theoretical curve calculated from Equation 22.

Values of β, determined from Experiments 1–3, where HTO was either gained or lost by the liquid phase at constant volume, varied only between 5.75×10^{-6} and 6.32×10^{-6} cm./sec. The value of S in Experiment 4 is related to β by $\beta = -SP_T{}^0/P_W{}^0$; therefore, the equivalent value for β is 5.1×10^{-6} cm./sec., which also agrees well with other values of β.

Basin Study

The chemical separations facilities at the Savannah River Plant routinely discharge very low-level liquid radioactive waste to earthen seepage basins. This waste is largely evaporator condensate and contains a large fraction of the fission product tritium from spent fuel elements. Monthly, water is taken from a depth of 1 ft. at one location in each basin, and the tritium content determined. After years of use, one of these basins (13,000 m.^{2} in area) became so impermeable that it was isolated from further discharges. During the three-year study on this isolated basin, the depth of water fluctuated between 450 and 376 cm. because of rainfall and evaporation, but was 409 cm. at both the beginning and end of the study (Figure 7). These conditions provided the opportunity to measure β under SRP environmental conditions without the difficulties encountered in a basin that continually receives waste containing varying concentrations of tritium.

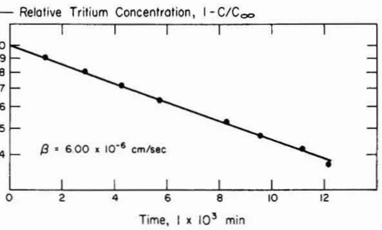

Figure 4. Relative tritium concentration in water when H_2O-saturated air containing HTO flowed across water surface

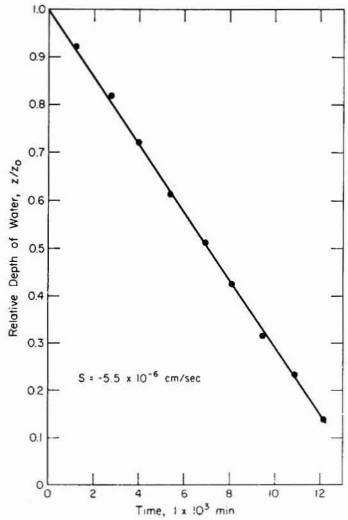

Figure 5. Depth of water remaining as dry air flowed across water surface

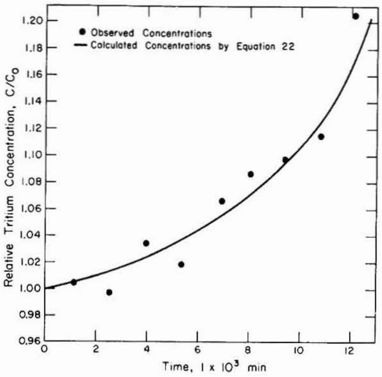

Figure 6. Relative tritium concentration in water as dry air flowed across water surface

As shown in Figure 8, the concentration of tritium in the basin water decreased at the 1-ft. depth. The rate of decrease was most rapid during the first seven months of measurements. This rapid tritium decrease seems to be caused by surface dilution from abnormally high rainfall and slow mixing of the surface layer with the underlying liquid. The normal annual

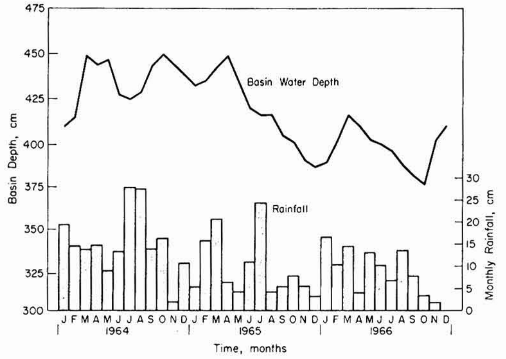

Figure 7. Depth of water in an isolated impermeable basin containing tritium and the rainfall received from January 1964 through December 1966

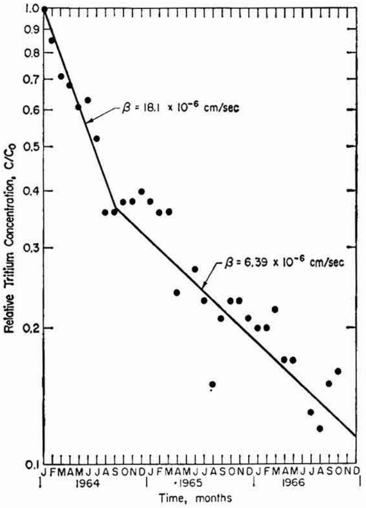

Figure 8. Tritium concentrations in an isolated impermeable basin from January 1964 through December 1966

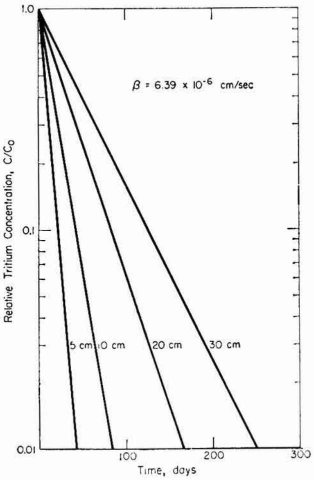

Figure 9. Relative tritium concentration remaining in several depths of water after exposure to air, as calculated with use of Equation 18

rainfall is 114 cm., however, during the first seven months of this study, rainfall totaled 140 cm. The slow mixing is caused by the slight specific gravity difference between the waste containing a small amount of salt and rain. The fairly constant tritium concentration from August 1964 to March 1965 tends to confirm that the rain was mixing very slowly with deeper water. This apparent slow mixing rate does not satisfy one of the specified conditions for our equations. Where mixing is slow but at a constant rate, the value of β will depend upon the rate of mixing and will be different for each rate.

If the periods January to September 1964 and September 1964 to December 1966 are considered separately (Figure 8), Equation 18 adequately describes the tritium concentrations. The straight lines drawn through the observed data were calculated by the least-squares method. The value of the transfer coefficient β was 18.1×10^{-6} cm./sec. for January to September 1964 and 6.39×10^{-6} cm./sec. thereafter. The latter value is considered the more accurate for normal conditions.

Tritium concentrations would be expected to vary greatly because of the wide variation in environmental conditions during the three-year period. Variations in wind velocity influence P_T; temperature influences P_T^0; and rainfall and evaporation influence the depth of water. Because environmental factors influence β, the values obtained at our basin are not applicable to other sites. However, the general principles discussed and demonstrated have wide applicability.

One conclusion of considerable practical importance, which may not be readily evident from either the laboratory or basin studies, is that exposing nuclear waste containing tritium to the atmosphere will decrease the tritium concentration of the waste under all likely environmental conditions. Tritium concentrations will decrease even when there is no rain to replenish evaporated H_2O, because, according to Equation 20, the relative humidity must be $<8\%$ for the tritium concentration to increase.

Applications

At some facilities, fission product tritium could not be released to flowing streams without exceeding the maximum permissible concentration. Farrow (1961) suggested that tritiated water be released to the atmosphere by distillation into plant off-gas and released through the stack. The results of our study suggest that basins be used to transfer tritium to the atmosphere. This transfer could be accomplished by batch discharges or continuous flow into a basin.

For a batch discharge, the fractions of tritium (C/C_0) remaining in basins containing various depths of water after various times are shown in Figure 9. These fractions were calculated by Equation 18 with $\beta = 6.39 \times 10^{-6}$ cm./sec., and assuming no change in depth (rainfall equals evaporation). The time required to transfer a given fraction of the tritium to the atmosphere is directly proportional to the depth.

For a continuous flow through the basin, the fraction of tritium remaining in water will depend upon the flow rate and surface area of the basin, assuming rainfall equals evaporation. In Equation 18, the depth of water $z = V/A$, where V is volume and A is surface area. So, $\beta t/z = \beta tA/V$. Time in the basin is V/f, where f is the flow rate. Therefore, $\beta tA/V = \beta A/f$ and Equation 18 becomes

$$\frac{C}{C_0} = \exp(-\beta A/f) \tag{23}$$

With use of Equation 23, with $\beta = 6.39 \times 10^{-6}$ cm./sec., the concentration of tritium in the water flowing from basins of

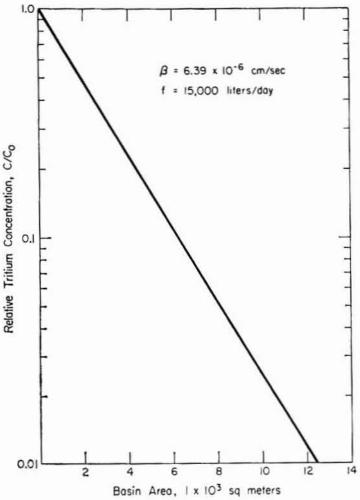

Figure 10. Relative tritium concentration in the effluent from a flow-through basin *vs.* basin area. Calculated with Equation 23

various cross-sectional areas was calculated for a flow rate of 15,000 liters per day. This flow rate was selected because it is equivalent to the volume of first-cycle condensate produced per ton of spent uranium during chemical separation as reported by Blomeke (1964). As shown in Figure 10, a basin area of 12,400 m.^{2} would be required to transfer 99% of the tritium to the atmosphere. To transfer 90% would require 6200 m.^{2} Although the surface area required is large, such a basin can be very shallow.

In any decision to divert tritium releases from flowing surface streams to the atmosphere, the impact of the change upon human radiation exposure must be evaluated. In many cases, tritium diverted to the atmosphere will result in reduced radiation exposure. Such decisions can not be made without considerable knowledge of the environmental conditions of the site in question.

Nomenclature

A = area, cm.^{2}
C = concentration of HTO in liquid, mmol./cm.^{3}
C_0 = value of C at $t = 0$, mmol./cm.^{3}
C_∞ = value of C at $dC/dt = 0$, or $\gamma/(S + \beta)$, mmol./cm.^{3}
dn_T/dt = rate of change in moles of HTO in the liquid phase under a unit area of surface, mmol./cm.^{2} sec.
dz/dt = rate of change of depth, cm./sec.
f = flow rate, cm.^{3}/sec.
i = subscript to refer to either component
K = proportionality constant, mmol. sec./g. cm.
m = number of moles of component transported per unit time and area from gas phase to liquid phase, mmol./cm.^{2} sec.
M_W = molecular weight of H_2O, g./mmol.
n = number of moles of component in liquid under a certain area, mmol./cm.^{2}
N_i = mole fraction of component i in solution, mmol./mmol.
P = partial pressure of component in vapor phase, g./cm. sec.^{2}
P^0 = equilibrium vapor pressure of pure component, g./cm. sec.^{2}
R = rate of rainfall, cm./sec.
S = dz/dt (constant), cm./sec.
t = time, sec.
T = subscript to refer to quantities related to HTO
W = subscript to refer to quantities related to H_2O
z = depth of liquid, cm.
β = $(KM_WP_T^0)/\rho$, or a value proportional to the rate at which C changes, cm./sec.
γ = KP_T, mmol./cm.^{2} sec.
ρ = density of liquid, g./cm.^{3}

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Atmospheric Technetium-99

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■ Technetium-99 has been isolated from 13 rain samples collected in 1967. The sizes of these samples were 53.5 to 233 liters. The concentrations of ^{99}Tc vary from 0.14×10^{-2} to 1.7×10^{-2} pCi/liter.

The natural terrestrial occurrence of technetium, as ^{99}Tc, has been established in pitchblende as a spontaneous fission product of ^{238}U (Kenna and Kuroda, 1961). This isotope has also been detected in rain (Attrep, 1962), in which it was assumed that the atmospheric ^{99}Tc is a fission product from nuclear detonations. A recent report by Golchert and Sedlet (1969) describes a radiochemical analysis of ^{99}Tc in water samples in which surface samples had an average concentration of 4.65 pCi/liter.

This report represents the examination of ^{99}Tc in a larger number of rain samples in order to confirm the atmospheric presence of this isotope. Among all the radioactive isotopes produced from nuclear detonations, ^{99}Tc has not been studied in detail. Since technetium as the pertechnetate ion behaves like iodide with respect to the thyroid system, it is worthwhile to establish the presence of ^{99}Tc in the atmospheric inventory of radioactive isotopes.

Large rain samples were collected over six months in 1967 and were examined for ^{99}Tc. The basic approach to the problem is similar to that of fallout studies of shorter-lived radioisotopes produced from nuclear devices detonated in the atmosphere. Due to its relatively long half-life ($t_{1/2} = 2.15 \times 10^5$ years), the activities of ^{99}Tc were expected to be low.

Experimental

For the radiochemical separation of ^{99}Tc from rain, samples ranging from 53.5 to 233 liters were taken. The samples were collected with a 3 m × 3-m rain collector located on top of the Science Building of East Texas State University in Commerce, Tex. Periodic cleanings of the collector and the polyethylene receptor were made with dilute nitric acid and distilled water.

Freshly collected rain was immediately acidified with nitric acid and stored in glass vessels until evaporation could be conducted. Prior to evaporation, the rain samples were made basic with sodium hydroxide to eliminate volatilization of technetium as Tc_2O_7. Rhenium, as ammonium perrhenate, was added as a carrier for technetium, and copper and molybdenum were also added. The evaporated concentrate was acidified and filtered. The residue was thoroughly washed. Hydrogen sulfide was passed through the hot solution 1 hr or longer. The sulfides were filtered, washed, and dissolved in ammonical hydrogen peroxide. The solution was evaporated to about 150 ml while keeping the solution basic at pH 8 or above. Alcoholic α-benzoinoxine was added and the precipitate was allowed to digest overnight at room temperature. The molybdenum α-benzoinoxine precipitate was filtered off and the pH of the solution was adjusted to precipitate the copper α-benzoinoxine. The copper precipitate was removed by filtration, and the filtrate again was reduced in volume. This filtrate was then passed through a cation-exchange column (Dowex 50W-×8, 100 to 200 mesh, H^+ form) and the column was washed with distilled water. The effluent was made basic and the volume was reduced to 50 to 100 ml, which was finally made 5*N* with respect to sodium hydroxide.

The pertechnetate and perrhenate ions were extracted into four 25-ml portions of methyl ethyl ketone. Chloroform, 125 ml, was added to the methyl ketone fraction and the pertechnetate and perrhenate ions were back-extracted with four 25-ml portions of distilled water. The aqueous fraction was made 2*N* with sulfuric acid, copper (II) was added, and hydrogen sulfide was passed through the hot solution for at least 1 hr. After filtration, the sulfides were dissolved with ammonical hydrogen peroxide and the solution was carefully reduced to 5 ml, keeping the solution basic. The solution was neutralized with nitric acid and loaded on an anion-exchange column (Dowex 1 × 8, 200 to 400 mesh, NO_3^- form, 1-cm i.d. × 20 cm), and then washed with a small portion of distilled water. The perrhenate

Table I. ^{99}Tc Concentrations in Rain Sample Collected at Commerce, Tex.

Collection date	Vol of rain, liters	^{99}Tc activity, pCi/liter
4/12 and 13/67 4/17 and 18/67 4/20 and 21/67	126	$(0.77 \pm 0.10) \times 10^{-2}$
4/25/67 4/30/67	100	$(0.22 \pm 0.22) \times 10^{-2}$
4/30/67 5/3/67	100	$(0.55 \pm 0.23) \times 10^{-2}$
5/3/67 5/14/67	100	$(0.43 \pm 0.06) \times 10^{-2}$
5/14/67 5/20/67	100	$(0.23 \pm 0.03) \times 10^{-2}$
5/20 and 21/67	100	$(0.14 \pm 0.03) \times 10^{-2}$
5/20–22/67	53.5	$(1.7 \pm 0.3) \times 10^{-2}$
5/29 and 30/67	88.5	$(0.89 \pm 0.19) \times 10^{-2}$
6/22/67 6/30/67	100	$(1.4 \pm 0.2) \times 10^{-2}$
6/30/67 7/1/67	100	$(0.65 \pm 0.10) \times 10^{-2}$
7/1/67 7/3/67 7/13/67 7/15/67	165	$(0.63 \pm 0.10) \times 10^{-2}$
7/19/67 9/7/67	233	$(0.63 \pm 0.10) \times 10^{-2}$
9/14/67 9/20 and 21/67	151	$(0.18 \pm 0.03) \times 10^{-2}$

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[1] Presently serving in the U.S. Navy.

and pertechnetate ions were eluted with 0.25*M* sodium perchlorate at a flow rate of 0.5 to 0.6 ml/min at room temperature. The rhenium fraction was analyzed spectrophotometrically according to Kenna (1961). Copper (II) was added to the technetium fraction, which was acidified with sulfuric acid, and hydrogen sulfide was passed through the solution while heating for 1 hr. The sulfides were cooled, filtered, mounted, and counted. The chemical yields averaged 25%, based on the amount of rhenium recovered.

A reagent blank was conducted with the above procedure. The blank indicated no activity. It was then assumed that there was no contribution of activity from the reagents used.

Radioactive measurements were conducted on a Tracerlab Omniguard Low Level Beta Counter. The background of the counting system was about 0.3 cpm.

Results and Discussion

Identification of the ^{99}Tc activity is based on indirect evidence. The observed activity in the rain samples followed the chemistry of technetium. Because the activities of these samples were low, and the half-life is so long, customary identification is impossible. Samples were counted for over two years with no decrease in activity; this is expected from the long-lived ^{99}Tc.

The half-thickness of the 0.29 MeV beta particle of ^{99}Tc is 7 mg/cm^2 of aluminum for the counter employed in this investigation. For the most active samples, this experiment was conducted with use of aluminum absorbers. The results gave half-thickness values of 7 mg/cm^2 ± 1, even for activities about 0.5 cpm. With this evidence, it was assumed the observed activities of these technetium fractions are attributed to ^{99}Tc.

The experimental results of the ^{99}Tc activities are given in Table I. The concentrations of ^{99}Tc vary from 0.14×10^{-2} pCi/liter rain to 1.7×10^{-2} pCi/liter rain. The average ^{99}Tc concentration is 0.65×10^{-2} pCi/liter or 2.3×10^{9} atoms/liter. The 1961 and 1962 rain samples (Attrep, 1962) contained ^{99}Tc concentrations of the order 0.2×10^{-2} pCi/liter and 4.4×10^{-2} pCi/liter, respectively. These values are in agreement with the results reported here.

Although the activities of ^{99}Tc found in this investigation are low and appear negligible, respresenting no major environmental contamination, the significance of these results lies in the ability of detection as well as the confirmation of this isotope in the atmospheric environment. Attention has been brought to environmental ^{99}Tc in water samples by Golchert and Sedlet (1969). Some 150 1-liter naturally occurring surface water samples were analyzed in which approximately 80% of these results were below the detection limit of their analysis. Those remaining ranged from 0.5 pCi/liter to 49.4 pCi/liter with an average of 4.65 pCi/liter. These values are much greater than those reported here, and no comparison is made since the location of sample collection was not noted.

Since the availability and use of this fission produced nuclide have increased in recent years, it is interesting to note that ^{99}Tc is becoming widespread both in the atmosphere and in the natural water systems.

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Ultrafiltration for the Control of Recycled Solids in a Biological System

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■ The use of low-pressure ultrafiltration is described as a means of liquid-solids separation for a high solids activated sludge system. (The concentrated microbial system ranged from 20 to 30 grams per liter volatile suspended solids.) The experimental apparatus consisted of a completely mixed biological reactor from which the activated sludge was recirculated across ultrafilter membranes. The quality of the final effluent was monitored by measurements of chemical oxygen demand, total organic carbon, and phosphorus and compared with measurements of these constituents in the soluble portion of the reactor mixed liquor. Gel-filtration chromatography, used to determine the molecular size distribution of simple and macromolecules in the reactor mixed liquor and ultrafiltrate, showed a gradual accumulation of macromolecules of approximate molecular weights between 700 and 1200. The molecular size distribution in the ultrafiltrate ranged from approximate molecular weight 30 to 800. The effect of pressure ultrafiltration on the bio-mass, monitored by oxygen uptake studies, showed a net decrease in respiratory activity with time of ultrafiltration. The high solids microbial culture maintained 75 to 95% reduction of chemical oxygen demand. The overall chemical oxygen demand removal efficiency of the high solids ultrafiltration system, however, exceeded 98%.

During the past four years, concentrated activated sludge systems have been studied at Rensselaer Polytechnic Institute. The concentrated microbial systems under investigation ranged from 20 to 50 g/liter volatile suspended solids (vss). At these levels, microbial suspensions normally do not settle by gravity. Consequently, other means of separation have been investigated. The method found to be most effective in separating microorganisms from the final effluent was membrane ultrafiltration. This unit operation is defined as "the hydraulic pressure activated separation of solutions into their individual components by passage through synthetic membranes" (Michaels, 1968). The process is not new and has been used by biologists for the separation and concentration of large molecular-weight species such as proteins and polypeptides. The feature which made the process

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of interest to environmental engineers was the development of relatively high flux rate anisotropic membranes based on cellulose acetate polymers. These particular membranes have found wide application in the desalination field with reported flux rates of over 25 gal./day/ft^2 (Loeb and Manjikian, 1965). However, the operation, thus far, has received only minor attention as a separation device for biological waste treatment.

Operationally, ultrafiltration (UF) is a simple process. A solution under pressure flows over a supported membrane. Under the impressed pressure gradient across the membrane, solvent and certain solute molecules pass through the membrane and are collected as ultrafiltrate. Larger molecules are retained by the membrane and a concentrated solution of retained molecules (retentate) is recovered from the feed water stream.

This paper describes a feasibility study on the use of ultrafiltration as a liquid-solids separation device for a high solids activated sludge system. The following were studied: (*a*) the flux rate through various membranes, (*b*) the quality of the final effluent from the ultrafilters, (*c*) the approximate molecular size range of dissolved solute in the mixed liquor and ultrafiltrate, and (*d*) the effect that the pressurized ultrafiltration system had on the respiration rate of the microbial culture.

Apparatus and Procedure

A schematic diagram of the activated sludge–ultrafiltration system is shown in Figure 1. The experimental apparatus consisted of a completely mixed, air-sparged, 10-liter reactor to which was connected a sludge recirculation line containing three ultrafiltration cells. The cells were supplied by Dorr-Oliver Inc. (Stamford, Conn.). Each cell contained a Dorr-Oliver IOPLEX membrane which measured 15.1 × 4.4 cm and had an effective area of filtration of 47.0 cm^2. In batch studies, using a feed water stream containing 2000 mg/liter of sucrose (molecular weight 354) the membranes retained 55% of the sucrose at a pressure gradient of 50 psig. The reactor was loaded at a process loading of 0.2 g of chemical oxygen demand per gram of VSS per day with a sterile substrate composed of 17.2 g/liter of glucose, 6.7 g/liter of ammonium acetate, 4.85 g/liter of ammonium dibasic phosphate, and 1.5 g/liter of yeast extract. This loading was sufficient to maintain a VSS concentration in the reactor of approximately 25 g/liter. Substrate addition was controlled at the rate of 2.0 liters per day by a T-8 series Microflow SIGMAMOTOR pump. Due to membrane area limitations, the liquid detention time in the reactor ranged from three to four days.

Daily samples of mixed liquor and ultrafiltrate were taken. The mixed-liquor sample was centrifuged at 20,000 rpm for 10 min to remove the suspended bacterial solids. The supernatant obtained was then analyzed for chemical oxygen demand (COD), total organic carbon (TOC), and phosphate. Since the membranes retained all the bacterial solids, the ultrafiltrate or effluent was analyzed directly for COD, TOC, and phosphate. The technique of gel-filtration chromatography was used to determine the approximate molecular size distribution of simple and macromolecules in the reactor mixed liquor and ultrafiltrate. The system was studied at three different ultrafiltration pressures—35, 50, and 75 psig—to determine the influence of pressure on solvent and solute flux rates. The reactor itself was not pressurized. The ultrafiltration system was pressurized by the combination of recirculation pump and a throttling valve located downstream from the UF cells. Pressure increases were made sequentially—i.e., the system was operated at low pressure for a period and then the system pressure increased. The effect of retentate accumulation and the possible effect of pressure on the viable cell mass were monitored by Warburg respirometer studies.

Results and Discussion

Flux Rates. The recorded flux rates from the three membranes are shown as a function of pressure in Figure 2. The solution flux rate is directly related to the applied pressure on the membrane barrier. The points plotted represent flux measurements after 24 hr of recirculation at a particular applied pressure. Initial flux rates were generally 20 to 25% higher than the 24-hr flux rates. The flux decline during this period is attributed to an initial compaction of the membrane film when pressure was applied.

Flux declines also are attributed to polarization effects such as the buildup of sludge cake and other solute material on the membrane. Since a feed water stream was used which contained 2 to 3% suspended solids (bacteria) the most significant polarization problem is the decreased water flux due to solids accumulation or cake formation on the upstream side of the membrane. Earlier work by the authors and by Okey and Stavenger (1966) has shown that the sludge cake formation can be prevented by maintaining turbulent flow conditions across the membranes. For these UF cells, fluid velocities over 3 ft/sec were necessary to maintain turbulent flow. The associated problem of dissolved solid precipitation and gel-layer formation on the membrane was not considered in these studies. In the present study, fluid velocities over 5 ft/sec were maintained by recirculating the activated sludge across the membranes at 3.5 gal./min. Therefore, no sludge accumulation was observed on the membrane films and flux rates remained relatively constant after the initial

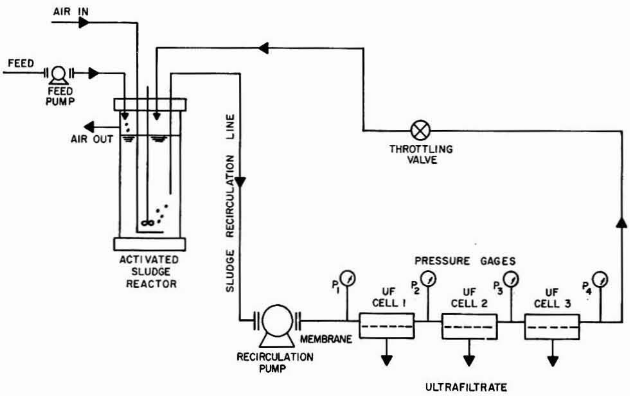

Figure 1. High solids activated sludge: ultrafiltration unit

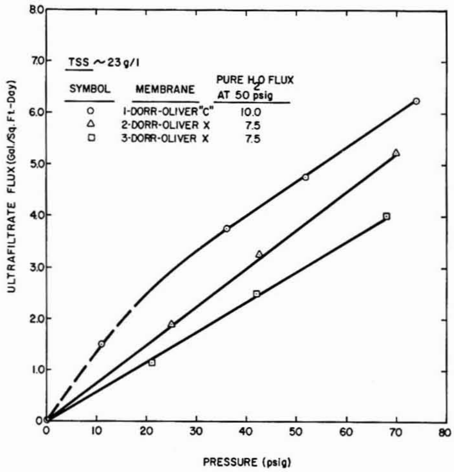

Figure 2. Ultrafiltration of high solids activated sludge at 25 °C

decline. The data showed that at an applied pressure of 50 psig to UF cell 1, the flux rate was 4.6 gal./day/ft^2, which was increased to 6.9 gal./day/ft^2 at 75 psig. Flux rates from membranes 2 and 3 were somewhat lower at the above applied pressures. These particular membranes were cut from a different stock sheet of Dorr-Oliver membrane and apparently had a tighter polymeric cross section.

Solute Flux. The relative rate of diffusion of solute through the membrane was determined by measuring COD and phosphorus in the mixed liquor and in the ultrafiltrate. The COD in the "soluble" portion of the mixed liquor and in the membrane ultrafiltrate are tabulated in Table I. The TOC of these fractions also is recorded. A gradual increase in the mixed liquor COD was noticed during the course of the study. The reason for this increase is thought to be a result of the membrane separation system. As shown in Figure 3, the membranes retained approximately 90 to 95% of the soluble mixed liquor COD. Since the process loading factor (food/mass) of 0.2 was used in the study, respiration was most likely in the endogenous range. Food entering the reactor, therefore, was used predominantly for energy requirements, with no net increase in bio-mass by synthesis. This condition was representative of the reactor system, since VSS determinations showed no increase in solids, but a decrease in volatile solids from 26.4 g/liter to 19.6 g/liter during the study period. Evidently, there was an accumulation of cell lysis products of high molecular weight which was retained by the membranes. This accumulation, which was confirmed by gel chromatography, is responsible for the observed increase of the soluble mixed liquor COD in the reactor system.

Due to the increase of COD in the mixed liquor, it is difficult to distinguish between the effects of solute concentration and pressure on the transfer of solute through the membranes. The data do show an apparent reduction in solute retention with increases in the pressure gradient. This effect is shown in Figure 3, where percent of COD retention is plotted against ultrafiltration flux rate. There is also indication (Table I) that the concentration of solute in the mixed liquor affected the solute concentration in the ultrafiltrate. The data for the second pressure system (50 psig) are representative of this influence; the mixed liquor COD increased, which resulted in a corresponding increase in the ultrafiltrate COD. This observation is not in agreement with the kinetics of solute retention by diffusive-type ultrafiltration membranes. (The Dorr-Oliver membranes used in this study are considered diffusive-type since the distilled water flux was 10 gal./day/ft^2 at a pressure gradient of 50 psig. Microporous membranes would show substantially higher water permeabilities.) It has been shown by various investigators (Merten, 1965; Michaels, 1968) that solute retention is not influenced by fractional solute concentration and increases rather than decreases with increasing flow rate during ultrafiltration. Since the membrane retains a portion of the solute in the solution driven through the membrane by the pressure gradient, the convective flux of solute toward the membrane will initially exceed the rate at which solute passes through the membrane (Michaels, 1968). The solute, therefore, will accumulate on the upstream face of the membrane, resulting in the phenomenon termed concentration polarization. The transport of solute through the membrane is influenced by the conditions at the immediate boundary layers—i.e., the upstream and downstream face of the membrane and transport will reflect the solute and solvent transport rates characteristic of the more concentrated polar-

Table I. Daily Reactor Mixed Liquor and Ultrafiltrate Solute Concentration[a]

Day	Reactor mixed liquor				Ultrafiltrate (membrane 1)			
	COD	TOC	T-PO$_4$	O-PO$_4$	COD	TOC	T-PO$_4$	O-PO$_4$
	mg/liter				mg/liter			
35 psig pressure system								
1	1425	200	3000	2750	246	28	2000	1950
2	2305	250	4300	3825	115	19	2900	2800
3	2540	270	4700	4075	115	18	3600	3100
50 psig pressure system								
4	3315	375	6600	5200	381	50	4025	3300
5	2945	325	8500	7125	176	28	6250	5150
6	4210	395	5200	4750	300	30	5200	3550
7	5370	405	5000	4300	495	35	4800	3500
75 psig pressure system								
8	6000	410	4950	4150	570	37	4800	3505

[a] Influent COD = 23,500 mg per liter × 2 liters per day = 47,000 mg per day.

ized layer. If the membrane is not completely solute impermeable, more solute will permeate the membrane, and retention will be lower. Concentration polarization may have been responsible for the observed decrease in retention of soluble COD. However, with the data reported here and the type of system studied, it is difficult to confirm this effect.

In the system reported here, the biological reactor is responsible for the removal of COD from the influent substrate. The membranes served to separate the bacterial solids from the reactor mixed liquor. These membranes, by their more open structure compared to reverse osmosis membranes, will not retain the low molecular weight intermediates produced by the activated sludge culture. These materials will permeate the membrane and exert COD in the final effluent or ultrafiltrate. The soluble COD retention effected by the membrane was predominantly the retention of high molecular weight products of cell lysis. These materials could conceivably accumulate on the upstream face of the membrane, thus producing a secondary membrane more impermeable to the low molecular weight metabolic intermediates. In this case, retention efficiencies might increase, but a secondary effect would also occur—that is, a reduction in water permeability through the membrane. In this study, a decline in water flux was not noticed for the period of the investigation and it is thought that secondary membrane formation did not occur.

Phosphorus. The phosphorus retention by the membrane was determined by measuring the soluble total and soluble orthophosphate in the mixed liquor and ultrafiltrate. The membranes retained about 30% of the orthophosphate at the 35-psig pressure system which decreased to about 18% retention at the 75-psig pressure system. Increases in mixed liquor orthophosphate concentration produced corresponding increases in the ultrafiltrate. Total phosphate analyses showed some permeation of polyphosphate through the membranes. The retention of polyphosphate again decreased as the system pressure increased and the concentration of polyphosphate increased in the reactor mixed liquor.

At the highest system pressure (75 psig) the polyphosphate concentration was higher in the ultrafiltrate than in the reactor mixed liquor. The polyphosphates in the reactor mixed liquor were the result of the biological activity since no polyphosphate was added to the system as substrate.

Molecular Size Distribution

The approximate molecular sizes in the reactor mixed liquor and ultrafiltrate were determined by gel-filtration chromatography. The gel columns were packed in Sephadex laboratory columns 2.5-cm i.d. × 100-cm long (Pharmacia Fine Chemical, Inc.). Sephadex G-10 (particle diameter 40 to 120 μ) or Bio-Gel P-2 (200 to 400 mesh) were used to pack the columns. Experiments were performed with the columns eluted with $0.01M$ KH_2PO_4 buffer. The flow rate through the Sephadex G-10 column was maintained at 60 ml/hr (1.2 ml/cm^2/hr) and through the Bio-Gel P-2 column at 40 ml/hr (0.8 ml/cm^2/hr). The eluant from the column was collected in 5-ml fractions with a LKB Radirac fraction collector in a cold room at 3°C. The respective fractions were analyzed for organic carbon using a Beckman Infrared Carbon Analyzer.

Generally, a 5-ml sample of reactor mixed liquor, previously centrifuged at 20,000 rpm for 5 min, was applied to the column for fractionation. To obtain readable fractions of ultrafiltrate samples, it was necessary to concentrate these samples. Concentration was done by vacuum rotary evaporation at a temperature of 40°C ± 2°.

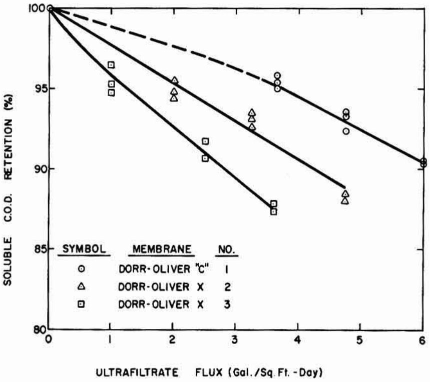

Figure 3. Retention of the soluble mixed liquor COD on Dorr-Oliver membranes

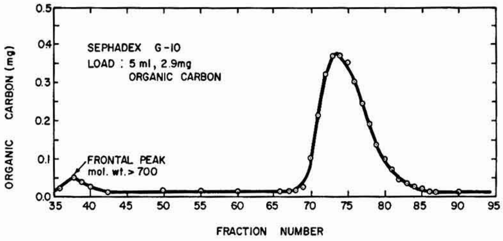

Figure 4. Elution profile of reactor mixed liquor before recirculation over ultrafiltration membranes

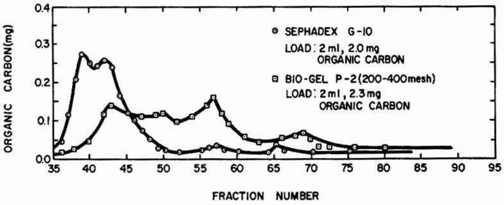

Figure 5. Elution profile of reactor mixed liquor after six days of recirculation over ultrafiltration membranes

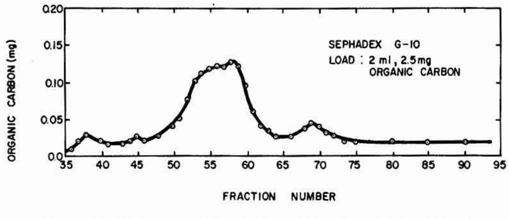

Figure 6. Elution profile of ultrafiltrate from membrane 1

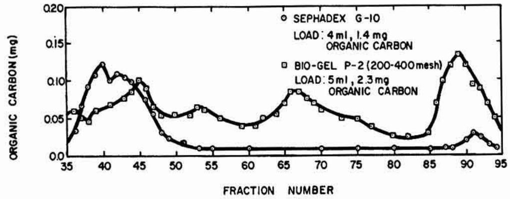

Figure 7. Elution profile of mixed liquor from activated sludge reactor allowed to accumulate waste products for 50 days

The determination of molecular weight was made from a plot of elution volume vs. log molecular weight (Determann, 1968). The elution volumes for known molecular weight compounds, therefore, were determined. The columns used in this study were standardized with use of a solution of Blue Dextran 2000 (Pharmacia Fine Chemical; mol wt, 2×10^6), raffinose (mol wt, 594), glucose (mol wt, 180), and acetic acid (mol wt, 60). Blue dextran was eluted at fraction number 38 for the Sephadex G-10 column and at fraction number 32 for the Bio-Gel P-2 column. In this manner the fronts or exclusion limits of the respective columns were defined.

The results of the study showed a gradual accumulation in the reactor of molecules in the 700 to 1200 mol wt range. This was determined by first fractionating reactor mixed liquor samples on Sephadex G-10 which has an exclusion limit of mol wt 700. Figure 4 shows the elution profile of the reactor mixed liquor before recirculation through the UF cells. This chromatograph represents a three-day accumulation of waste products, during which time the reactor was fed continuously. A small frontal peak at fraction number 38 indicates a small percentage of molecules greater than mol wt 700. Figure 5 shows the reactor mixed liquor after six days of recirculation. A significant increase in the height of the frontal peak is observed indicating a gradual accumulation of larger molecular weight species. The same sample was fractionated on Bio-Gel P-2 which has a reported exclusion limit of mol wt 1600. No frontal peak was observed, but a peak at fraction number 42 was representative of approximate mol wt 1200 (Figure 5).

A Sephadex G-10 chromatograph of ultrafiltrate is shown in Figure 6. The majority of solute was found to be in the mol wt range of 100 to 400. Fractionation of the ultrafiltrate on Bio-Gel P-2 showed that the mol wt 1200 fraction in the mixed liquor was retained by the membranes and that the largest size molecule permeating the membrane was approximately mol wt 800.

To confirm that cell degradation products will accumulate in an activated sludge reactor if sludge wasting is not practiced, a completely mixed reactor was studied for 50 days. During this time, no effluent was removed from the reactor. The MLVSS were maintained at approximately 10 g/liter. The feed entering the reactor was identical in composition to that used for the ultrafiltration study. The feed rate was adjusted to equal the evaporation loss from the reactor and thereby the liquid volume in the reactor was kept approximately constant at 8 liters. A sample of the mixed liquor after 50 days operation of this reactor (previously centrifuged to remove the suspended solids) was fractionated on Sephadex G-10 and Bio-Gel P-2. The resulting chromatographs (Figure 7) showed that there was an accumulation of molecules in the mixed liquor of mol wt 700 to 1400. This size range was indicated by the frontal peak at fraction number 38 on the Sephadex chromatograph which represented molecules of mol wt greater than 700, and a peak at fraction number 36 on the Bio-Gel chromatograph which represented molecules of approximate mol wt 1400. Fractionation of DIFCO yeast extract on Sephadex G-10 showed that the yeast extract component of the substrate does contain some molecules of mol wt greater than 700, approximately 19% by weight. However, a mass balance on the amount of dissolved high molecular weight material in the reactor system and that which was added via yeast extract showed that the accumulation of high molecular weight material in the mixed liquor could not be accounted for by the yeast extract addition. It is suspected, therefore, that the majority of this material represents products of cell lysis.

Oxygen Uptake Rate

The respiratory activity of the viable cell mass was measured to observe whether the accumulation of the large molecular weight molecules had a toxic effect and (or) if the pressure recirculation had an adverse effect on the culture. The initial oxygen uptake rate (K_R) for the culture before recirculation was 20 mg O_2 per gram vss per hour. At the end of three days recirculation at 35 psig, the K_R decreased to 18 mg O_2 per gram vss per hour. Pressure was then increased to 50 psig and maintained for three days. At the end of this period, the K_R dropped to 7 mg O_2 per gram vss per hour. During this period, the MLVSS decreased from an initial concentration of 30 g/liter to 20 g/liter, after which the vss remained constant for the remaining study period (48 hr). Since ultrafiltration membranes completely retain bacterial solids (Hindin *et al.*, 1968; Ironside and Sourirajan, 1967), the loss in volatile suspended solids may be accounted for by cellular lysis. The death of cells could be attributed to the low process loading, toxic effects, and possible destruction of cells by the recirculation system. The exact cause of the decreased activity of the culture cannot be determined at the present time but it is believed that toxicity may be a major factor (Young, 1969).

Discussion

A feasibility study for the use of ultrafiltration as a separation device for a concentrated microbial system has been described. The average ultrafiltrate flux rate was 4.5 gal./day/ft.^{2} The data show that the high solids activated sludge-ultrafiltration system consistently removed 97 to 99% of the COD in the influent feed water. Since the ultrafiltration membranes retained soluble organic molecules of approximate mol wt greater than 800, there occurred a gradual accumulation of cell degradation products in the reactor system. This material may have an inhibiting affect on the viable cell mass.

From the results to date, it is concluded that ultrafiltration is a highly effective means of separating microbial solids from final effluent. The method also allows more effective control of food/mass ratio and sludge wasting than by conventional clarification or centrifugation methods.

With the development of higher flux rate membranes and a better understanding of the effects of solute retention and the effects of pressure on the microbes, ultrafiltration may become an integral part of biological waste treatment systems of the future.

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Alkaline Scale Abatement by Carbon Dioxide Injection

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■ Distillation of untreated seawater results in precipitation of alkaline scaling compounds (calcium carbonate and magnesium hydroxide) on heat transfer surfaces. Scale deposition was successfully eliminated by continuous injection of carbon dioxide in an experimental evaporator. Threshold carbon dioxide levels for scale control increase with distilling temperature and range from 37 ppm at 255°F to 64 ppm at 284°F. Profiles of carbon dioxide concentration, pH, and scale composition were studied over a wide temperature range. Special techniques were developed for injection of carbon dioxide and monitoring the concentration in a pressurized system. Methods were also worked out for collection and analysis of scale deposits. Carbon dioxide injection offers advantages over acid injection or polyphosphate-based additives which are currently used for controlling alkaline scale.

Control of alkaline scale in boilers dates back to 1821 when it was found, by accident, that potato starch materially reduced the rate of scale accumulation (Payen, 1823). Since that discovery, numerous scale control techniques have emerged. Reviews of the state of the art are presented by Badger (1959), McCutchan and Glater (1964), and recently by Elliot (1969). Approaches to the scale problem have varied from pure empiricism, approaching folklore, to a sound application of scientific principles. Two leading methods in use today are addition of blended additives such as Hagevap (Liddell, 1957) and injection of mineral acid (Checkovich, 1964; Zuckerman, 1967). Hagevap is limited to low-temperature evaporators and does not completely restrict scale accumulation. Total elimination of scale may be accomplished by acid injection, but under these conditions high corrosion rates have been observed. Both methods increase product water cost by about three cents per thousand gallons.

Alkaline scale consists of calcium carbonate and magnesium hydroxide, separately or in mixtures. The predominant compound depends on operating conditions and to some extent on the type of distilling equipment. Both scale forms result from thermal decomposition of bicarbonate ion present in all natural waters, and the amount of alkaline scale is dependent on bicarbonate ion concentration (McCutchan *et al.*, 1966). This, in turn, is related to solution pH, as shown in the equation

$$CO_2 + H_2O \rightleftarrows H^+ + HCO_3^- \rightleftarrows 2H^+ + CO_3^{2-} \qquad (1)$$

As pH is lowered, equilibrium is shifted to the left, in favor of carbon dioxide. The fractional distribution of carbonate species in seawater as a function of pH is given in Figure 1. This chart is based on pK values for carbonic acid in seawater (Buch, 1938). At pH values below 4, dissolved carbon dioxide becomes the major species in solution. In distilling plants that use acid injection, attainment of equilibrium is speeded up by removal of carbon dioxide in degassing equipment. Ideally, bicarbonate is completely destroyed by this process and the brine pH rises above 7. In practice, however, good control of acid injection is difficult, and this operation sometimes causes excessive plant corrosion.

Failure to remove bicarbonate results in thermal decomposition of this ion and subsequent precipitation of alkaline scaling compounds. A mechanism for scale formation was proposed by Hillier (1952) and modified by Langelier (1954). At temperatures below 180°F, calcium carbonate is precipitated according to the equations

$$2HCO_3^- \overset{\Delta}{\rightleftarrows} CO_3^{2-} + H_2O + CO_2(g) \qquad (2)$$

and

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3 \qquad (3)$$

At higher temperatures, the rate of carbonate hydrolysis increases markedly, and a competing series of reactions can occur which results in the formation of magnesium hydroxide

$$CO_3^{2-} + H_2O \rightleftarrows CO_2(g) + 2OH^- \qquad (4)$$

$$Mg^{2+} + 2OH^- \rightleftarrows Mg(OH)_2 \qquad (5)$$

The initial step in alkaline scale formation (Equation 2) will be driven to the right by removal of carbon dioxide gas. From the laws of chemical equilibrium, we know that bicarbonate decomposition is restricted by increasing the partial pressure of carbon dioxide in the system. The shift in equilibrium under these conditions can also be explained by pH alteration. From Figure 1 it is apparent that carbonate ion cannot exist in solution below pH 7 at 20°C. Increasing the partial pressure of carbon dioxide in contact with seawater causes the pH to drop far below this level through formation of carbonic acid (Sverdrup *et al.*, 1942). At higher temperatures, lower pH values are required to inhibit scale formation. This is illustrated by the modified Langelier stability diagram (Figure 2). Scaling thresholds for calcium carbonate are based on concentration factor and pH, and are described by a family of lines of variable total alkalinity. The single, bold, sloping line delineates scaling thresholds for magnesium hydroxide which are dependent on pH and solution concentration only. Areas to the right of any line represent supersaturated conditions. The temperature scale was derived from a linear correlation of Langelier's data at two temperatures. Although a linear assumption may not be absolute over this temperature range, the graph clearly shows that lower equilibrium pH values are needed to inhibit scale at higher temperatures.

The injection of carbon dioxide into natural waters and aqueous solutions has been used in several industrial applications dating back about 50 years. Herrero (1923) used carbon dioxide from stack gases to increase the solubility of barium carbonate in the "lime-barium" water softening process. Injection of carbon dioxide has also been used to improve the recovery of sodium carbonate from natural brines (Hightower, 1951). A similar application to offshore sulfur mining by the Frasch process was successful in minimizing scale formation in pipes carrying hot seawater (Cockrell, 1959). Bradstreet (1950) attempted to increase the

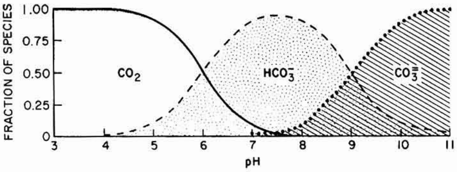

Figure 1. Carbonate species in seawater as a function of pH

ratio of calcium carbonate to magnesium hydroxide scale in an experimental evaporator by distilling seawater previously saturated with carbon dioxide. Instead of this expected result, he was surprised to find the total amount of scale was reduced by 65%, and the deposit consisted of pure magnesium hydroxide. No explanation was offered for his observation, and this line of experimentation was discontinued. Hickman (1958) added crushed Dry Ice to feed water for a centrifugal distillation apparatus. Previously formed scale dissolved rapidly and equipment performance was restored to its initial level.

McCutchan and Glater (1964) suggested further study of carbon dioxide injection into seawater as a mechanism for alkaline scale prevention. Several papers on scale control with carbon dioxide have since appeared in the literature. These include a proposal by Cadwallader (1967), a patent by Checkovich (1965), and pilot-plant studies by the Atomic Energy Commission ("Desalting Digest," 1968).

Suppression of alkaline scale was demonstrated by McCutchan and Glater (1965, 1966) with small volumes of natural seawater in laboratory glassware. Based on the successful outcome of these experiments, it was decided to extend this work to a dynamic system closely approximating conditions in an actual flash evaporator. An experimental heating loop with a single flash chamber was constructed and studied intensively to evaluate the feasibility of alkaline scale abatement by carbon dioxide injection.

Apparatus

All experiments were conducted with filtered natural seawater hauled by truck from Marineland, Palos Verdes, Calif. It was therefore necessary to build a small system to minimize the volume of water required. The final apparatus contained a single evaporator tube and was designed to process 45 gallons per hour under continuous flow conditions.

Essential components of the apparatus consisted of a metering pump, carbon dioxide injection vessel, concentric tubular heat exchanger, and flash chamber (Figure 3). A glass window for scale observation was provided at the high-temperature end of the parallel flow heat exchanger. A flash chamber was also constructed from borosilicate glass pipe so that visual observations could be made. The heat exchanger was designed to carry steam inside a 3/8-in. o.d. brass tube. Seawater was passed through the annulus formed by this tube and an outer brass tube of 5/8-in. o.d. with a wall thickness of 0.005 in. Overall length of the heat exchanger was approximately 11 ft. Compression fittings and Teflon ferrules were used at all joints so the inner heat transfer tube could be removed easily for examination or collection of scale samples.

The apparatus was equipped with pressure gauges, flow meters, and thermocouples at locations shown in Figure 3. Frequent measurements at these positions provided good process control. During all experimental runs, seawater back-pressure was maintained above the saturation vapor pressure so that boiling did not occur in the heat exchanger. Hot seawater was throttled into the flash chamber through

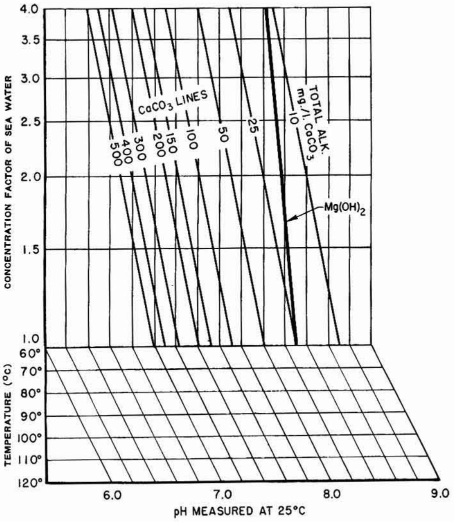

Figure 2. Stability diagram for calcium carbonate and magnesium hydroxide in seawater brines (adapted from Langelier, 1950)

a stainless steel needle valve, and flashing was induced by venting steam from the chamber. During all experimental runs, heat transfer coefficients, chamber flashdown, and nominal temperature differences were maintained close to those of a conventional flash evaporator.

Initial calibrations with tap water were performed to test the soundness of equipment, check instrumentation, and establish thermal performance. A constant water flow of 0.75 gallon per minute corresponding to a velocity of approximately 2.3 ft/sec was maintained and used in future experimental runs. This figure was close to the upper limit of our equipment design. Although somewhat lower than figures reported in the literature, it was considered a representative velocity from a scaling standpoint. The apparatus performed smoothly over an outlet water temperature range of 195° to 270°F. Water temperature was found to increase linearly with inlet steam pressure. Overall heat transfer coefficients were consistent with values reported in the literature for similar heat exchangers including multistage flash condenser tubes. Calculated values ranged from 636 Btu/ft^2, hr, °F at 50 psig inlet steam pressure to 670 Btu/ft^2, hr, °F at 79 psig. Nominal temperature differences between 18° and 28°F were determined over the temperature range of interest in this study.

Scale Formation from Natural Seawater

Initial experiments were performed to test the feasibility of depositing scale in the equipment on a single pass without brine recycle. All runs were performed with natural seawater, pH values ranging from 7.9 to 8.3, and ambient temperatures from 75° to 83°F. To study scaling capability, seawater was heated in the equipment at various temperatures for different test durations. Scale was observed through the tube sight glass in less than 20 min at an outlet water temperature of 277°F. During a 1-hr run at 216°F, the entire heat transfer tube was coated with a thin layer of gelatinous scale. The successful outcome of these experiments was beyond expectation and demonstrated the practicality of depositing measurable scale in short time periods with relatively small volumes of seawater.

A series of 1-hr runs was carried out between 187° and 277°F to determine quantitatively scaling characteristics of the equipment. Temperature, pressure, and pH values were monitored while visual observations were made for scaling in the heat exchanger and flash chamber. All pH measurements were carried out at 25°C. Scale formed on the heat transfer surface first in small spots which grew rapidly until the entire surface was coated. The onset of scaling took less time as water temperature was increased, but visual detection of the exact time of initial deposit was difficult and tentative. A more exact evaluation of scaling was accomplished by chemical means.

After each run, the heat exchanger was dismantled and scale samples collected from the heat transfer tube. Deposits were dissolved separately from inlet and outlet ends by immersing a fixed tube length in a measured volume of one normal hydrochloric acid for 3 min. The acid solutions were filtered and analyzed for calcium and magnesium ion by atomic absorption spectroscopy. This analytical technique is free of interference by traces of copper and iron in the acid solutions. Results are expressed as mg of calcium carbonate or magnesium hydroxide per in.^{2} of heat transfer surface. Samples of suspended scale were also collected from the flash chamber and discharge brine by filtering standard volumes of slurry, dissolving the precipitate in acid and analyzing for calcium and magnesium.

Operational and analytical data for all scaling runs are presented in Table I. Scale samples were predominantly magnesium hydroxide, as predicted by Hillier (1952), and scaling intensity was shown to increase with outlet water temperatures. This phenomenon (Figure 4) can be explained on the basis of increasing supersaturation with respect to scaling compounds as the temperature is elevated. The rate of nucleation is known to depend on the level of supersaturation. In contrast to the definite trend in quantity of magnesium hydroxide deposited, calcium carbonate values were essentially constant in all experiments, varying between 0.02 and 0.04 mg/in.^{2} The small amount of calcium was probably an impurity and not due to deposition of calcium carbonate scale. More likely, dissolved calcium and magnesium salts crystallized from residual brine as water evaporated when the tube was removed and dried at the completion of each experiment. To determine the extent of this impurity, the standard length of clean heat transfer tube was dipped in seawater and allowed to dry. Analysis of the residue gave blank values equivalent to calcium carbonate and magnesium hydroxide of 3.3×10^{-2} and 9.4×10^{-2} mg/in.,^{2} respectively. Since experimental calcium carbonate values are close to this figure and vary within reasonable experimental error, scale deposits were evidently pure magnesium hydroxide. Corrected values for this compound can be obtained by subtracting 9.4×10^{-2} mg/in.^{2} from recorded data.

Magnesium hydroxide was also identified in slurry samples from the flash chamber. Trends in variation of scale quantity with temperature were difficult to evaluate since solid was distributed between chamber walls and suspended material. Flashdown temperatures ranged between 5° and 10°F, and had little effect on the amount and composition of suspended scale. Values of pH in the flash chamber were 0.2 to 0.7 unit higher than seawater feed because of thermal decomposition of bicarbonate ion. Discharge water contained an even thicker suspension of magnesium hydroxide than flash chamber samples because of the additional carbon dioxide loss. pH values rose only slightly higher, however, since hydroxide ion was simultaneously consumed in forming the precipitate.

The presence of calcium sulfate scale was never established in samples from the heat transfer surface, flash chamber, or discharge water. This was an expected result since operation was conducted in a region unsaturated with respect to calcium sulfate hemihydrate even in the 280°F temperature range. The literature is quite confused with regard to calcium sulfate scaling thresholds, but approximate temperature limits for hemihydrate and anhydrite in unconcentrated seawater are 300° and 250°F, respectively. Although potential anhydrite saturation was achieved in high-temperature runs, this compound could not precipitate because of short residence time in this apparatus. It was reported by Langelier *et al.* (1950) that equilibrium occurs first with hemihydrate and conversion to anhydrite is a very slow process. Unpublished work in this laboratory has shown a sharp increase in transition rate at elevated temperature, but at 280°F, we would not anticipate anhydrite scale in a single pass evaporator with residence time less than 1 min. This prediction was confirmed by our experiments.

During all scaling runs, thermal performance was observed to decline with operating time. Scale buildup is reflected in a gradual decrease in outlet water temperature resulting from insulation of the heat transfer surface. The extent of scaling is related to the rate of decline in outlet water temperature. Plots of water temperature *vs.* time for two initial outlet temperatures are shown in Figure 5. The onset of thermal decline corresponds with initial nucleation of scale crystals which are at this time invisible. Change in thermal performance is therefore a more sensitive indicator of scaling than just visual observation.

After each run, equipment was reassembled and the entire heating loop cleaned by circulating an inhibited acid solution at 140°F and rinsing with tap water. Traces of remaining scale were removed from the inner tube by cleaning with fine steel wool.

Scale Abatement by Carbon Dioxide Injection

Experiments were conducted to evaluate carbon dioxide injection as a means of alkaline scale abatement. Conditions were parallel to preceding experiments except that all runs were conducted above 250°F, so that potential scaling conditions were more severe. Carbon dioxide was metered into a mixing chamber through a small fritted-glass sparger at pressures well above feed seawater pressure in the system. The absorption of gas took place rapidly at full flow conditions, and design of the mixing device did not prove critical. Steady-state brine concentrations between 6 and 64 ppm of carbon dioxide were easily achieved and maintained throughout these experiments.

The relationship between carbon dioxide concentrations and pH is shown in Figure 6. Carbonated water samples were collected just downstream of the injection vessel and pH was measured within 1 min to minimize errors from possible gas evolution. Since final pH readings are sensitive to ambient levels, three arbitrary curves were drawn representing initial pH values of 8.00, 8.15, and 8.30. For a fixed initial pH value, the pH variation with log of carbon dioxide concentration is nearly linear. Since both scales are logarithmic, progressively larger absolute increases in carbon dioxide concentration are required to lower pH as the resultant pH declines.

Experiments were conducted at temperature levels in the mid-250°, 260°, 270°, and 280°F ranges at various carbon dioxide concentrations. Chemical and physical measurements for these runs are shown in Table II. As in preceding experiments, scale on the heat transfer surface was essentially pure magnesium hydroxide. Calcium sulfate scale was never observed even at 284°F. From Figure 7, it can be seen that scale deposition falls off rapidly as carbon dioxide concentration is increased. In the mid-250°F temperature range, scale accumulation can be drastically reduced at carbon dioxide injection levels of approximately 10 ppm. Although scale reduction is clearly demonstrated by chemical data, the decline in outlet water temperature remains about the same as in untreated seawater. Evidently, a thin layer of magnesium hydroxide is nearly as good an insulator as a thick layer, and, from a practical standpoint, complete scale elimination is mandatory. By gradually increasing the level of injected carbon dioxide, a point was reached where thermal performance did not deteriorate during the standard 1-hr run. Threshold carbon dioxide levels determined in this manner for three temperatures are presented in Table III. In each of these runs, the heat transfer tube was "clean" by visual examination, and chemical analysis for magnesium hydroxide gave values of the same order as the blank determination.

Scale prevention by carbon dioxide injection may be considered to begin when magnesium hydroxide approaches a "zero rate of deposition." Under these conditions seawater would not be sufficiently supersaturated to cause deposition of this compound on heat transfer surfaces. Increasing carbon dioxide concentration beyond this "zero precipitation" threshold should result in a "negative rate" of scale deposition. This idea presents the possibility of dissolving alkaline scale at higher-than-threshold levels of carbon dioxide. A test of this hypothesis was carried out by deliberately scaling the equipment during a 40-min run at an initial outlet water temperature of 270°F. During this period, temperature dropped to 256°F (Figure 8), and rapid scale growth was observed through the sight glass. Carbon dioxide was then injected at a concentration of 52 ppm, which caused a drop in pH to 6.51. This carbon dioxide level arrested further scale growth and caused a stabilization of outlet water temperature at about 255°F. Evidently these operating conditions were close to the scaling threshold or zero rate of scale deposition. After 30 min, carbon dioxide concentration was increased to 149 ppm which caused the pH to level off at 6.0. This caused an immediate and rapid rise in outlet water temperature and scale deposits were observed to dissolve. Within 10 min at pH 6.0, outlet water temperature returned to 268°F, and the heat transfer surface was almost scale-free.

During carbon dioxide injection runs, considerable frothing was observed in the flash chamber due to evolution of injected carbon dioxide. Bicarbonate decomposition was also in evidence since pH values rose far above feed water levels. This occurred in spite of the short residence time in the chamber (approximately 1 min) and the small flashdown temperature range. Magnesium hydroxide was identified on chamber walls and in brine slurry samples. It was observed that carbon dioxide runs generated larger amounts of scale in the flash chamber than corresponding scaling runs at the same temperature levels. This could be expected since little or no scale was deposited in the heat exchanger. Although magnesium hydroxide precipitated rapidly from solution, steady-state conditions were not achieved in a single flash chamber. As in the scaling experiments, additional magnesium hydroxide was suspended in discharge samples and brine pH values rose to slightly higher levels.

Discussion

Alkaline scale accumulation is eliminated in the heat transfer loop of a flash evaporator by injection of carbon dioxide. In unconcentrated seawater, scale is prevented at temperatures up to 284°F by maintaining the feed pH below 6.4. This required injection of carbon dioxide to a concentration between 50 and 68 ppm, depending on the original pH. These levels will vary with total alkalinity, ionic strength, and magnesium content of a water sample.

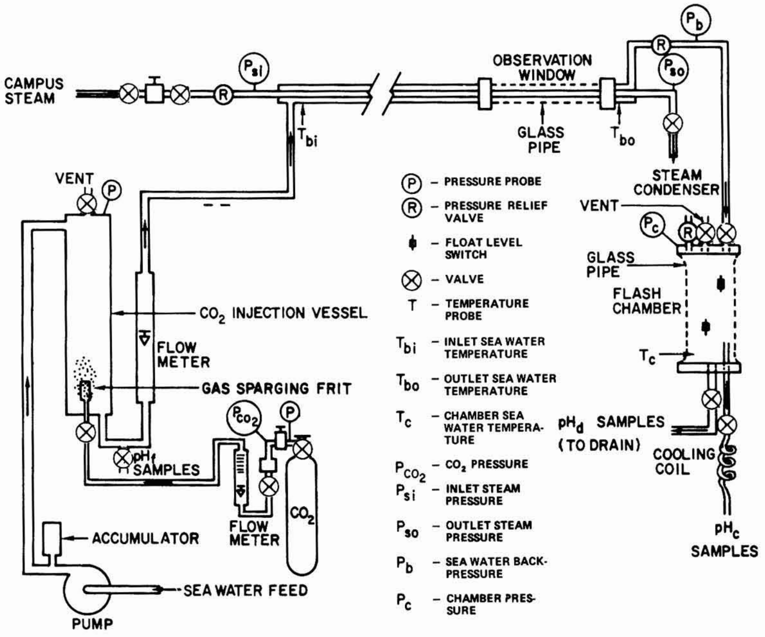

Figure 3. Schematic diagram of experimental heating loop

Table I. Alkaline Scale Deposition during Scaling Runs with Natural Seawater[a]

Run duration, hr	Initial outlet water temp., T_{bo}	Initial outlet nom. temp. diff., $T_{si} - T_{bo}$	Magnesium as $Mg(OH)_2$, mg/in.^{2}	Calcium as $CaCO_3$, mg/in.^{2}	Total decline in outlet water temp.
1.5	187	. .	13.6×10^{-2}	1.90×10^{-2}	5
1.0	197	. .	16.3	2.28	. .
1.0	212	21	19.9	2.86	5
1.0	226	22	33.0	3.04	8
1.0	234	20	41.7	3.44	8
1.0	250	20	95.9	3.95	10
1.0	277	24	141.0	3.04	23

[a] Seawater flow rate: 0.75 gal./min; seawater backpressure: 30 to 70 psig; inlet seawater temperature range: 73° to 80°F; scale samples collected from outlet end of heat exchanger; temperatures measured in °F.

Carbon dioxide injection may prove to be a practical alternative to acid injection, which is currently favored in flash plants. This system would grossly reduce the cost of water treatment chemicals because carbon dioxide could be recycled without the requirement for additional makeup. Recycle with minimum loss of process efficiency is made possible by the very rapid evolution of CO_2 at elevated temperatures. More carbon dioxide is generated from bicarbonate decomposition than the amount needed for injection. Based on a stoichiometric conversion of 140 ppm bicarbonate in unconcentrated seawater, it would be possible to recover about 100 ppm CO_2. This is in excess of the 64 ppm required for scale abatement even at 284°F.

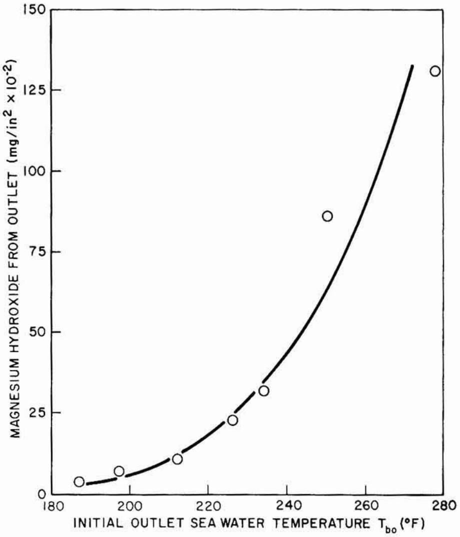

Figure 4. Magnesium hydroxide scaling as a function of temperature

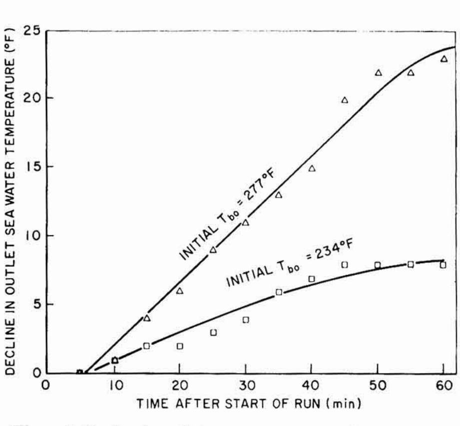

Figure 5. Decline in outlet water temperature due to scaling

Reduced corrosion is another advantage of this system. Since carbon dioxide is a weak acid, accidental overdosing will not cause dangerously low pH conditions. Furthermore, the release of carbon dioxide during flashing results in high pH values. This should significantly reduce steel corrosion rates from the brine stream as it passes through flash chambers. In addition, carbon dioxide can be used as a convenient, safe, cleaning method for plants incrusted with alkaline scale.

Further development of this technique should emphasize investigation in three important areas. First, it will be necessary to determine the effect of evolved carbon dioxide on venting and corrosion within flash chambers. Since carbon dioxide is released very rapidly, venting rates must be increased in the first few stages. If the evaporator is operated above atmospheric pressure, this may be accomplished with little difficulty. Although flashing brine should produce little corrosion, the corrosive process must be considered in the chamber vapor space where carbon dioxide is released. Both proper venting and control of noncondensable corrosion require further study and assessment.

Second, attention must be given to the capability of recovering carbon dioxide stripped from the brine. It should be determined if economical reuse of carbon dioxide is feasible. If the concentration of other noncondensables vented in the hottest chambers are kept low, recycling should not be a difficult problem.

Third, the nature and effect of scale precipitation in the flash chambers after pressure release is of critical importance. Since the driving force for crystallization is the spontaneous loss of carbon dioxide from bulk brine during flashing, precipitation will be favored in bulk solution. This tendency will be strengthened by the fact that the walls of the flash chamber do not act as heat-transfer surfaces. Ideally, turbulence in the brine stream would be strong enough to carry suspended particles as a slurry and dislodge any significant buildup of soft, gelatinous magnesium hydroxide on vessel surfaces. Practically, however, this is a matter for further study, and the effect of scale slurries and wall growths on plant performance should be examined. More work is needed to establish profiles of pH and precipitated solids in a series of flash chambers.

Table II. Alkaline Scale Deposition during Carbon Dioxide Injection Runs with Natural Seawater[a]

Run duration, hr	CO_2 concn, ppm	pH after CO_2 injection, pH_f	Initial outlet water temp., T_{bo}	Initial outlet nom. temp. diff., $T_{si} - T_{bo}$	Magnesium as $Mg(OH)_2$, mg/in.^{2}	Calcium as $CaCO_3$, mg/in.^{2}	Total decline in outlet water temp.
1.0	6.0	7.77	253	28	87.2×10^{-2}	4.94×10^{-2}	11
1.0	13.3	7.24	256	24	26.8	4.00	9
1.0	37.0	6.72	255	23	14.5	3.23	0
1.0	6.0	7.80	266	23	89.5	4.75	10
1.0	10.3	7.71	262	26	24.9	3.23	9
0.8	22.0	7.20	263	25	24.3	2.86	3
1.0	29.0	6.88	261	24	18.3	3.04	3
1.0	6.0	7.47	276	23	108.8	5.91	10
1.0	17.3	7.10	276	21	26.5	2.66	5
1.0	27.0	7.00	275	23	21.6	3.04	7
1.0	38.0	6.77	275	25	15.4	3.42	4
1.0	52.0	6.48	273	23	21.2	4.19	0
1.0	64.0	6.40	284	21	12.3	3.23	0

[a] Seawater flow rate: 0.75 gal./min; seawater backpressure: 70 psig; inlet seawater temperature range: 73° to 83°F; CO_2 line pressure: 88.2 psig; scale samples collected from outlet end of heat exchanger; temperatures measured in °F.

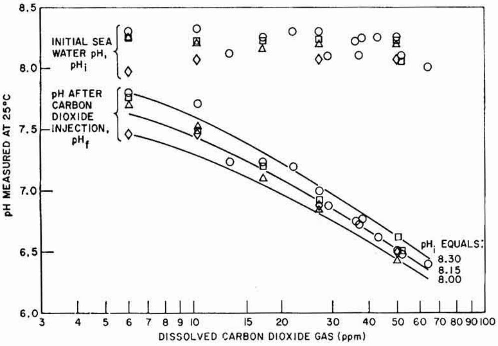

Figure 6. Seawater pH as a function of carbon dioxide concentration

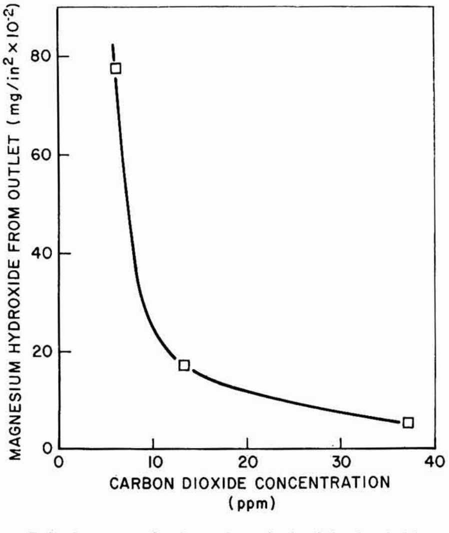

Figure 7. Scale suppression by carbon dioxide injection (initial outlet water temperature range, 253° to 256°F)

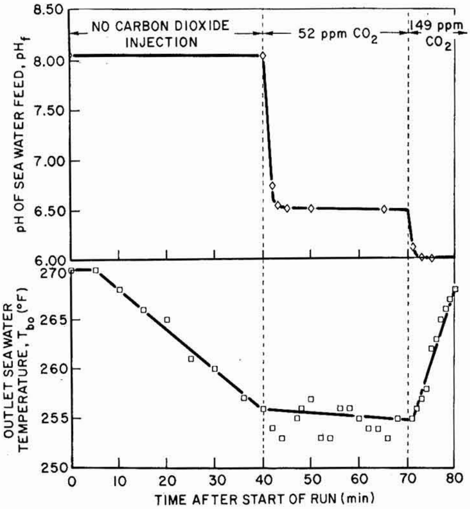

Figure 8. Thermal performance as a function of carbon dioxide concentration

Table III. Threshold Carbon Dioxide Levels for Alkaline Scale Abatement in Three Distilling Temperature Ranges

Initial outlet seawater temp., T_{bo}, °F	Carbon dioxide concn, ppm	pH after carbon dioxide injection, pH_f	Final outlet seawater temp., T_{bo}, °F
255	37	6.72	255
273	52	6.48	273
284	64	6.40	284

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COMMUNICATIONS

Continuous Monitoring of Water Surfaces for Oil Films by Reflectance Measurements

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■ Laboratory experimentation and plant tests have shown that the use of reflectance measurement is a promising means of continuously monitoring water surfaces for oil contamination. The instrument resulting from these experiments is both simple and sensitive and can be used as a qualitative analyzer which would sound an alarm if oil slicks of significant size are detected.

Recent concern over the possible pollution of public waters by floating oil has led to the need for an oil film detector which could be used at critical points on water streams or surfaces to announce the presence of an undesired slick.

Simple first-order calculations, based on Snell's law and the Fresnel equations (Vašíček, 1960), reveal that the reflection of unpolarized light from an oil surface ($n = 1.40$) should occur with about 50% greater intensity than from a water surface ($n = 1.33$), for angles of incidence in the 5° to 30° range. All hydrocarbon materials which may be considered "oils" have refractive indexes of at least 1.39, and a means for detecting oil on water is suggested therein.

A laboratory arrangement consisting of an incandescent lamp, collimating lens, and photodetector was used to generate a light beam incident on a water surface and to measure the intensity of the reflected beam. The measured average intensity, using an angle of incidence of 30°, increased 100% when a drop of "waste oil" was introduced on the water. Without filtration, the electrical signal was found to vary rapidly from zero V dc to a certain maximum value due to surface turbulence, which caused the reflected beam to swing back and forth across the detector. The actual intensity increase is significantly greater than the calculated value. This is possibly due to multiple internal reflections and light absorption in the oil film because thin films of oil on water give rise to more reflected light than very thick films. The lower limit of detectability is not known, but it is probably a function of the oil's color, its tendency to form a uniform film, and other properties.

A prototype oil film monitor (Figure 1) was constructed for tests of the reflectance principle in a refinery effluent stream. The apparatus was constructed in a housing which was safe for refinery usage, and consisted of the components listed in Figure 1. The device was floated on a waste water stream (flowing at 1 ft/sec) and the actual reflectance measurement was performed continuously at a point (B) beneath the

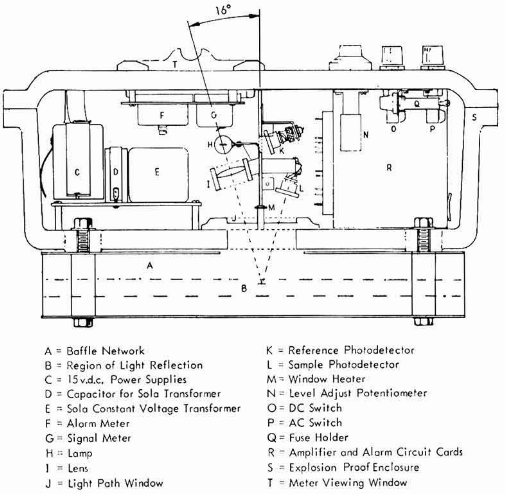

Figure 1. Prototype oil-on-water monitor

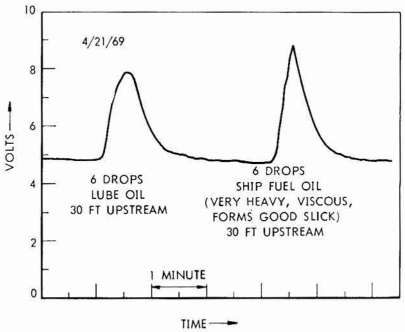

Figure 2. Response to oil films on an effluent water stream

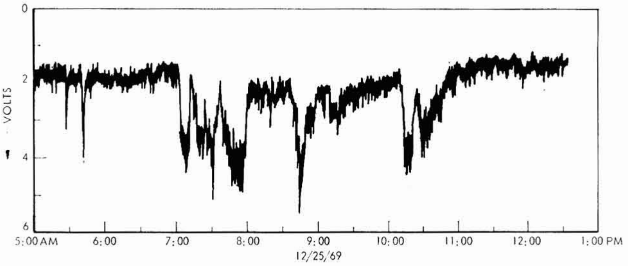

Figure 3. Response to oil films on estuary water

instrument, inside a baffle used to calm the water. The basic measurement was made with a solid-state photodetector in a Wheatstone bridge circuit with a reference detector. The signal was amplified with conventional operational amplifier circuitry, and signal "noise" was rendered insignificant with use of a 5-sec time constant resistance/capacitance filter. A typical record of instrument response to an oil film obtained during a three-week test is shown in Figure 2; signals from significant oil slicks were generally eight times greater than noise or drift, and thus, a preset level detector could easily detect signal changes due to oil. Water temperature, salinity, and turbidity changes have little effect on the behavior of the instrument, and water flow rate changes of two or three factors also have a negligible effect.

Adaptation of this measurement principle to use in open waters susceptible to tidal fluctuations, exaggerated wave action, high winds, large flow direction and rate changes, and miscellaneous floating solids has met with success in a two-month test. A peak picking electronic circuit was used in place of the RC averaging to improve response, and Figure 3 shows the reaction of the device to a large oil slick. The most severe problem is that of maintaining a clear window (above the water surface) through which light passes. In tests of an experimental apparatus at a tanker loading dock, the window was located 6 in. above the water, at the top of an airtight chamber open only at the bottom. It is not known how far above the water it is feasible to locate such a window, but with it 6 in. above the surface, fouling reduced response to oil about 50% in six to eight weeks. Although reaction to an oil slick, once it enters the baffle, is immediate, the subsequent action taken (such as an audible alarm) can be delayed electronically if desired, so that only slicks of consequence are "detected."

Hallikainen Instrument Co., Richmond, Calif., has been licensed by Shell Development Co. to manufacture the oil-on-water monitor. A model suitable for refinery effluent streams is available, and Hallikainen is currently considering the necessary modifications in the design to make an instrument suitable for use in the more harsh environment prevalent in large open bodies of water.

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Analysis of Barium Sulfate by Atomic Absorption

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■ A novel, simple method for analyzing total airborne barium collected in high-volume samples with use of atomic absorption spectrometry is described. The reducing potential of filter paper on barium sulfate is utilized to reduce quantitatively the insoluble barium compound to acid soluble barium sulfide.

Barium-containing smoke suppressants have been suggested as a possible solution to the problem of smoke-emitting, diesel-powered vehicles. The barium additive is blended in small quantities into the diesel fuel before its use. In addition to the need for evaluating the barium additive as a smoke suppressant, the toxicity of barium compounds in the exhaust (Sax, 1957) must also be considered. Concomitant with field testing of the barium-containing suppressant in a fleet of New York City buses, airborne particles were collected with use of a high-volume sampler and analyzed for total barium content (soluble barium compounds and insoluble barium sulfate).

Analysis for total barium content has been performed by emission spectroscopy with a 1.5-m direct-reading spectrograph (Curry, 1969). This method produces satisfactory results, but requires expensive equipment and highly trained personnel.

This communication describes a novel, simple method for analyzing total barium in high-volume samples by atomic absorption spectrometry. Chemical preparation of the samples is simple, quantitative, and the instrumentation is inexpensive and easy to operate. This analytical procedure utilizes the reducing potential of filter paper on barium sulfate, a phenomenon which has long been recognized (Pierce et al., 1959; Rieman et al., 1951). The manner in which small quantities of barium sulfate collected on a paper matrix can be quantitatively reduced to acid soluble barium sulfide is also described.

Experimental

Instrumentation. Barium concentrations were determined with a Jarrell-Ash fully compensated atomic absorption spectrophotometer equipped with a Jarrell-Ash laminar-flow burner. This instrument incorporates all logic and command circuits necessary for automated sample presentation and concentration readout. It uses two monochromators which space-share the hollow cathode light that passes through the flame. The monochromators also time-share light that bypasses the flame, and subsequent electronic circuits correct light variations. The automatic instrument consists of a specimen handler (accommodates up to 200 samples), an aspiration probe, a preconcentrator system, a sequencer/programmer unit, a concentration computer/digitizer, and a teletype paper tape punch. The analyses were performed by using the 4555 Å spectral line in conjunction with a fuel system of nitrous oxide–acetylene.

Although the instrumentation used in these analyses is highly automated because of the nature of some of the other work performed in these laboratories, any recognized model atomic absorption spectrophotometer can be used.

Sample Collection. Airborne particles were collected on 8 × 10-in. Schleicher and Schuell 589 green ribbon paper mats with a high-volume sampler. One portion of this high-volume sample was used to analyze solution barium compounds while the other portion was used to analyze the total barium content (soluble barium compounds and insoluble barium sulfate).

Analytical. Three types of barium samples were analyzed. In one case, a known volume of a solution of barium chloride was pipetted on 14 in.^{2} of filter paper, followed by dilute sulfuric acid treatment to convert all of the barium to barium sulfate.

In a second case, 1000 μg of solid barium was weighed, transferred to 14 in.^{2} of filter paper, and then analyzed for barium. In the third, portions of high-volume samples collected at a diesel bus fuel stop were analyzed for barium by the atomic absorption technique, and these findings were compared with the results obtained with a direct-reading spectrograph (Curry, 1969).

CASE 1. Solutions (1 ml) prepared from Baker and Adamson reagent-grade $BaCl_2 2H_2O$ containing 250, 500, and 1000 μg/ml of $BaCl_2$ were pipetted onto a 14 in.^{2} (2-×7) strip of Schleicher and Schuell 589 green ribbon paper. The papers were then treated with 2 ml of dilute sulfuric acid solution (5-to-1). The samples were dried again at 110°C, and finally 0.5 g of ashless powdered filter paper (W. R. Balston Ltd.) was placed as a blanket over the samples. Platinum crucibles containing the samples were ashed in a muffle furnace for 0.5 hr at 350°C, followed by 1 hr at 600°C, and finally at 700°C for 1 hr. The ashed samples containing the residues of 250, 500, and 1000 μg/ml of barium were treated with 5, 5, and 10 ml of Mallinckrodt Transist AR-grade nitric acid (1-to-3), applying heat as necessary to complete the dissolution. The resulting solutions were carefully heated on a hot plate to near dryness, transferred to volumetric flasks of appropriate capacity to keep the concentrations within the linear response of the instrument, and diluted to the mark. The 1000 μg/ml barium sample was diluted to 200 ml, the 500 μg/ml barium sample was diluted to 100 ml, and the 250 μg/ml barium sample was diluted to 50 ml. The solutions at this point are ready to be analyzed with the atomic absorption spectrophotometer.

CASE 2. Reagent-grade barium sulfate (1000 μg) was washed onto a 14 in.^{2} (2-×7) strip of Schleicher and Schuell 589 green ribbon paper and was placed in a platinum crucible. Fourteen runs were performed. The samples were dried at 110°C in an oven, ashed in a muffle furnace, and prepared for atomic absorption analysis in the same manner described in Case 1.

CASE 3. Airborne particles were collected at a bus fuel stop on an 8-×10 inch Schleicher and Schuell 589 green ribbon paper matrix, using a high-volume sampler (HEW, 1962) capable of handling 30 to 50 cfm of air sample. Of the 80-in.^{2} paper matrix used, 7-×9 in. (63 in.^{2}) were exposed to air

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sample. On each sample, a strip (10.1 in.^{2}) was cut from the exposed mat with use of a plastic cutting guide. The strips were folded into platinum crucibles, ashed, and chemically treated prior to atomic absorption analysis in the same manner as in Case 1.

A corresponding segment (4-×7 in.) of the same high-volume sample was wet-ashed with nitric acid–perchloric acid, followed by hydrogen peroxide, dissolved in nitric acid, and diluted with water for analysis. The analysis was performed utilizing the 4555 Å line of a Jarrell-Ash 1.5-m direct-reading spectrograph (Curry, 1969).

Results

CASE 1. When barium chloride solutions were converted to barium sulfate and then reduced to barium sulfide through the ashing technique, the recovery of barium was excellent. Several runs performed on samples containing 1000, 500, and 250 μg/ml of barium gave an average recovery of 100, 99, and 96%, respectively. The results are summarized in Table I.

Table I. Results of Recovery Experiment[a]

Run	Barium concn, μg	Recov. barium, %	Av % barium recov.	Standard deviation
1	1000	110		
2	1000	100		
3	1000	100		
4	1000	96	100	7
5	1000	98		
6	1000	100		
7	1000	110		
8	1000	89		
9	500	100		
10	500	101		
11	500	98	99	2
12	500	100		
13	500	96		
14	250	100		
15	250	96		
16	250	94	96	4
17	250	100		
18	250	92		

[a] Aqueous $BaCl_2$ converted to $BaSO_4$. Filter-paper ashing technique. Analysis by atomic absorption.

Table II. Results of Recovery Experiment[a]

Run	Recov. barium, %	Av % barium recov.	Standard deviation
1	96		
2	100		
3	99		
4	88		
5	94		
6	99	94	6
7	88		
8	100		
9	80		
10	98		
11	100		
12	93		
13	95		
14	88		

[a] 1000 g solid $BaSO_4$ added. Filter-paper ashing technique. Analyzed by atomic absorption.

Table III. Comparison of Analytical Results of 11 Samples Collected at Bus Fuel Stops

		Barium found on 63-in.^{2} matrix, μg	
Run	Total barium,[a] μg/m^3	Atomic absorption[b]	Direct-reading spectrograph[c]
1	1.27	153	158
2	0.83	104	90
3	1.43	199	160
4	1.27	134	138
5	1.18	156	132
6	5.1	946	706
7	8.6	1330	1040
8	6.1	841	851
9	13.0	1417	1531
10	20.1	2146	2337
11	8.2	1271	1254

[a] An average barium concentration of 0.03 mg/m^3 was reported from New York City's Aerometric network from June to December 1969.
[b] Reading represents the average of five runs of the original solution.
[c] Analysis performed utilizing the 4555 Å line of a Jarrell-Ash no. 66–000 Compact Atom Counter (1.5-m direct-reading spectrograph).

CASE 2. The recovery of 14 runs containing 1000 μg of solid barium sulfate was excellent. The average recovery for the 14 runs was 94%. Table II summarizes these results.

CASE 3. Total airborne barium collected with a high-volume sampler on 80- × 10 in. Schleicher and Schuell 589 green ribbon paper was analyzed by both atomic absorption and emission spectrography. The results agree well. There seems to be no high or low trend for either method. The results are summarized in Table III.

The Wilcoxan matched-pair signed rank test was used to determine whether the atomic absorption and the direct-reading spectrograph readings were the same. This test gives 23 for the sum of values of differences in which the direct-reading spectrograph was higher and 43 for differences in which the atomic absorption was higher. Since the critical value for a two-tail test at 5% risk is 11, it is evident that for this sample observations, the Wilcoxan test does not distinguish between the two methods. The two methods can therefore be considered comparable.

Discussion

The results obtained in all three cases demonstrate that insoluble barium sulfate can be determined by atomic absorption spectrometry when it is present in small quantities. Work is currently in progress to determine the upper limit for the determination of barium sulfate and, further, to explore the use of this reduction technique to other insoluble compounds.

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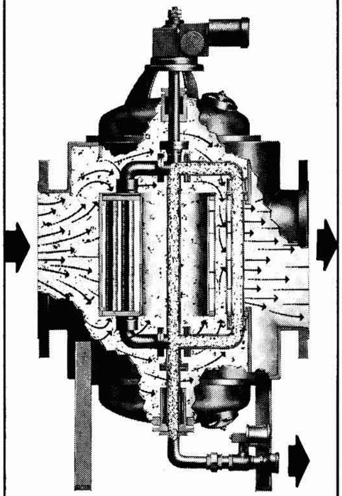


industry trends

Monsanto Enviro-Chem Systems, Inc. has been awarded a $29.7 million construction contract for expansion of the Rochester, N.Y., main sewage treatment plant. The expanded facilities will provide primary and secondary treatment and are part of an $80 million project to modernize all of Rochester's sewage facilities. Construction is to begin immediately and is scheduled to be completed at the end of 1973.

Calgon Corp. (Pittsburgh, Pa.) has acquired Havens International (San Diego, Calif.), a company with extensive experience in the reverse osmosis and ultrafiltration fields. Calgon is a wholly owned subsidiary of Merck & Co.

Great Lakes Chemical Corp. (W. Lafayette, Ind.) has acquired a majority stock interest in Natural Resources Management Corp. (Worthington, Ohio) for an undisclosed amount of cash. A division of NRM is engaged in drilling deep wells for liquid disposal and is equipped to carry out geological and engineering work. Great Lakes Chemical is a producer of bromine and bromine chemicals.

The American Oil Co. has placed on stream at its Sugar Creek, Mo., refinery a new unit that removes 80 tons of sulfur per day from fuel oil components and refinery fuel gases. The dual unit consists of a 27,000 bbl/day Ultrafiner which removes the sulfur and a second section in which the sulfurous compounds are converted to elemental sulfur.

Billings & Gussman, Inc. (Waltham, Mass.) has been formed to provide research and consulting services in the fields of air pollution control, aerosol technology, community and plant environmental surveys, and industrial hygiene engineering. The principals were formerly associated with Harvard Air Cleaning Laboratory.

Environmental Devices Corp. (Marion, Mass.) has announced expansion of its Survey Division operations. The division carries out ecological surveys to determine water quality and effects on it of industrial discharges. Particular emphasis is being placed on thermal discharges and their effect on aquatic life.

Dravo Corp. (Pittsburgh, Pa.) has designed and built a water treatment plant at the Chicago works of Republic Steel Corp. The plant removes particles of scale produced in a variety of hot rolling operations. Heart of the plant consists of 14 Dravo deep-bed filters.

Westvaco Corp. (New York, N.Y.) has been awarded a $350,000 contract by APCO-EPA to expedite the scale-up of a proprietary sulfur oxides removal process. The Westvaco process uses dry fluidized beds of granular activated carbon to convert sulfur dioxide and trioxide to elemental sulfur. The company is a large manufacturer of activated carbon.

Envirotech Corp. (Palo Alto, Calif.) has acquired the Allen Pump Co. (Paoli, Pa.), a manufacturer of materials handling centrifugal pumps. The pumps are designed for rigorous service applications. Envirotech now has five divisions serving the chemical and allied industries.

Jones & Henry Engineers Ltd. (Toledo, Ohio) has announced formation of a subsidiary firm called Jones & Henry Laboratories, Inc. The new firm has a laboratory devoted entirely to the analysis of waste waters. It will provide services for waste characterization, pilot plant studies, stream monitoring, and consultation.

PPG Industries Inc. (Pittsburgh, Pa.) will employ a Beckman hydrocarbon analyzer mounted on a mobile cart to monitor hydrocarbon emissions at plants in its Coatings and Resins Division. The first plant to be so monitored is one in Circleville, Ohio. Hydrocarbons are related to occasional odor complaints received by PPG.

Environmental Dynamics (Eugene, Ore.) is a newly formed nonprofit corporation which will undertake fundamental studies that are nationwide in applicability. The company expects to receive federal and private foundation funds. The initial thrust of the new firm will be in the field of solid waste management.

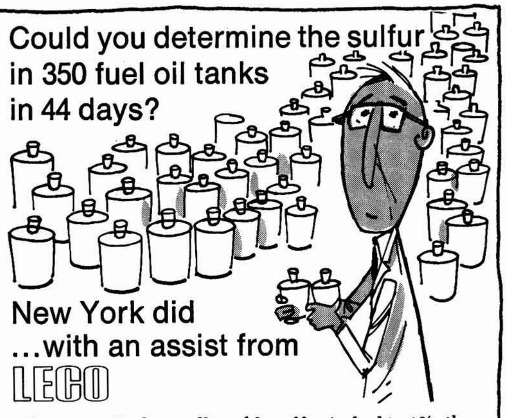
Vickers Petroleum Corp. (Wichita, Kan.) has completed a revamp of 40 acres of waste stabilization ponds at its refinery in Ardmore, Okla. Waste waters are held in the ponds for 130 days before discharge. The ponds have a total capacity of 29 million gallons.

The Foxboro Co. has opened a $250,000 waste treatment facility which handles all liquid pollutants at its Foxboro, Mass., plant. Separate waste streams are separately treated in the new plant, which (not surprisingly) is controlled by an instrumentation system designed by Foxboro.

Polymer Industries, Inc. (Greenville, S.C.) has installed a gas scrubber system manufactured by Schutte and Koerting Co. (Cornwells Heights, Pa.) at its specialty chemicals plant near Greenville. The scrubber–separator system and a vent gas scrubber system are used to prevent fumes and vapors from polymerization processes from being discharged to the atmosphere.

Western Gear Corp. (Lynwood, Calif.) will build, through a Florida subsidiary, a $2.7 million waste treatment system for the city of Calhoun, Ga. The system will handle 7 million gpd of waste. Calhoun is in the center of the large Georgia carpet industry. The same Western Gear subsidiary will build a $300,000 addition to the industrial waste treatment plant of a pulp and paper company in Palatka, Fla.

The B.F. Goodrich Chemical Co. (Akron, Ohio) will spend more than $200,000 to eliminate sulfur dioxide and particulate emissions at its plastics products plant in Marietta, Ohio. The elimination will be achieved by switching from coal to oil or gas as power generation fuel. Target date is mid-September 1971.



SOLID WASTES

A new publication of the American Chemical Society puts the nation's solid waste problems in perspective.

A 96-page book entitled "SOLID WASTES" contains 26 articles that first appeared in Environmental Science & Technology.

Among the topics covered are:

- Incineration
- Pyrolysis of plastics
- Electricity from waste
- Federal government programs
- Fly ash utilization
- Auto hulk disposal

and many others

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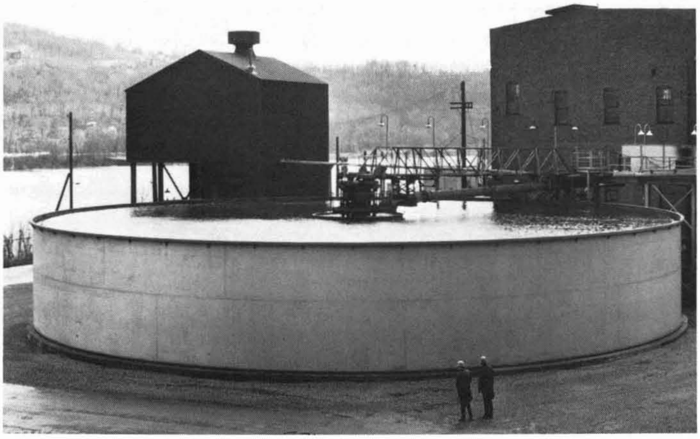
new products

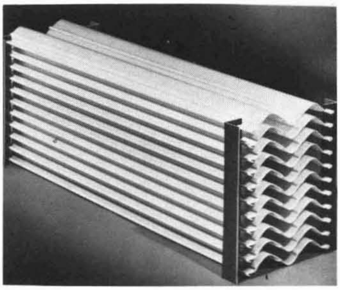


Magnetic flocculator

Clarification unit uses permanent magnets to speed settling of magnetic solids from slurries or liquids. Particles in waste water pass between the magnets, are themselves magnetized, and then attract each other to form flocs which settle out. Magnetic material is stable to −40°F and magnets are available in different strengths. Eriez Magnetics **61**

Thermal oxidizers

Direct thermal oxidizers convert effluent gaseous hydrocarbon or organic solvents to carbon dioxide. Units are applicable to any low air volume process—up to 1800 scfm—which discharges noxious effluents to the atmosphere. The DTO-M series consists of eight basic models handling a variety of air volumes. Conversion of pollutant is as high as 98%, the company says. Acrometal Products, Inc. **62**

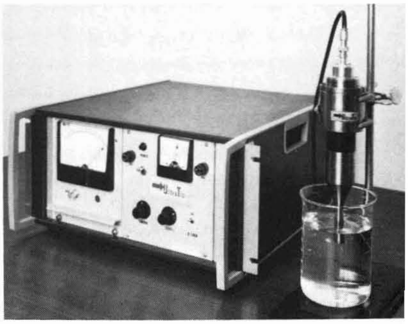


Mist eliminator blades

Corrosion resistant plastic blades can remove up to 99% of entrained liquid from gas or air streams. The blades are available individually in standard 12-ft. lengths or as factory-assembled modules. Units are lightweight and can be installed on roofs without additional supporting steelwork or the use of heavy-duty cranes. ABS or PVC construction provides good resistance to alkalai, acid, or other corrosive substances. Heil Process Equipment Corp. **63**

Cleaning agent

Ecologene is a phosphate-free, general purpose cleaner, stripper, and degreaser, which the manufacturer says offers no sacrifice in cleaning power. The product contains no enzymes, NTA, nitrates, or other plant nutrients and is biodegradable. Elgene Chemicals, Inc. **64**



Ultrasonic probe

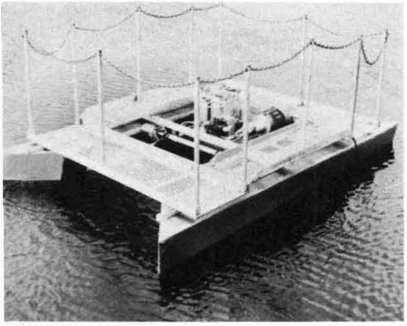
High-power ultrasonic probe, called UltraTip, is useful for declumping bacteria before ultraviolet decontamination of liquid streams, sludge aeration, liquid degassing, and emulsification. UltraTip operates at a nominal frequency of 23 kHz with electroacoustic efficiencies as high as 85%. The probe can be operated for extended periods of time. The unit features a wattmeter which measures true electrical power feed to the transducer under load. Wave Energy Systems, Inc. **65**

Ozone monitor

Self-contained, atmospheric ozone monitor measures ozone concentrations between 0.01 and 10.00 ppm. Air is continuously and automatically sampled and analyzed. The unit may be used in remote, unattended stations. The Model 1003 ozone monitor has a digital panel readout, with additional analog or binary-coded decimal output options available for interfacing with strip-chart recorder or computer. Dasibi Corp. **66**

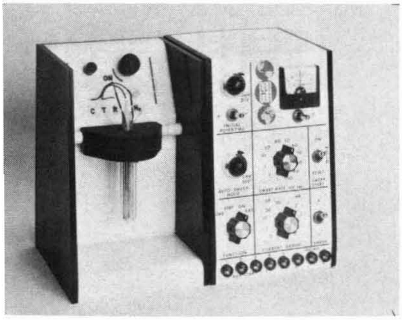
(continued on page 364)

(continued from page 363)



Oil recovery unit

Reclam-Ator separates oil from water with a foam-like material mounted on a rotating drum. The foam, which has a selective affinity for oil in water, is squeezed by a pressure cylinder, and oil, carrying little more than trace amounts of water, is diverted to a sump where oil can be pumped to a receiving vessel for disposal or recovery. Units are available for fix-mounted or float-mounted installations. Welles Corp. **67**



Metals analyzer

A compact, single cell, electromechanical unit measures concentration of lead, zinc, mercury, and several trace metals and organic chelates down to 0.01 ppb. With the addition of a battery pack, the detector can be used in the field. Additional accessories allow the instrument to be used as a polarographic device. Environmental Sciences Associates, Inc. **68**

SO$_2$ meter

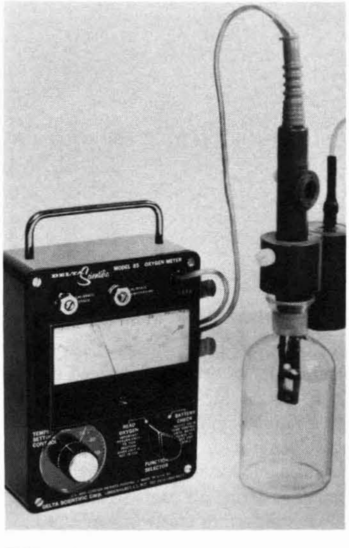
The Model U-2D sulfur dioxide monitor uses solid-state circuitry and substitutes plastic for glass to gain portability and ruggedness. The unit weighs four lb and operates with pen-cell batteries. Sensing mechanism, which does not use air pumps or liquids, measures ambient SO$_2$ concentrations in 0 to 0.5 ppm range. Combustion Equipment Associates, Inc. **69**

Oil absorbent

Controil, an expanded, surface-activated vermiculite, soaks up oil from water and will not release it even when thrown on a sandy beach. The material absorbs about four gal. of oil per cubic foot, is nonflammable, harmless to marine life, and will float on water for weeks. Pollution Control Products Corp. **70**

Fume scrubber

Lab-Air fume scrubber is capable of removing a wide variety of chemical and solution fumes from the laboratory. The unit removes 99% (where concentrations are below 1000 ppm) of such substances as hydrogen fluoride, perchloric acid, and bromine. The scrubber uses a packed-bed absorption column. Norton Co. **71**



DO meter

Dissolved oxygen and BOD tests can be done with the Model 85 dissolved oxygen meter in the lab or in the field without resorting to Winkler titrations. The meter probe has an automatic pressure compensator and can be used at depths up to 100 ft. The probe also has a built-in temperature sensor. Delta Scientific Corp. **72**

Ozone generator

AIROX ozone generators allow laboratory production of small quantities of ozone for experimentation or pilot plant operation. The air-cooled units operate on standard 115 V, 60-cycle current and are available in several sizes to produce from 3–18 grams of ozone per hour from dry air or oxygen. Pollution Control Industries, Inc. **73**

Dust control calculator

A plasticized cardboard metric duct calculator enables users to determine requirements for a complete dust control system. The calculator provides information about cubic meter per hour requirements and branch pipe sizes for metal and woodworking machines, duct and conveying velocities for several types of material expressed in meters per second, resistance losses of elbows and branches and conversion measurements for air flow from pipes of differing geometries. Torit Corp. **74**

Aeration unit

Static Mixer aeration unit can add as much as 50% more dissolved oxygen per horsepower hour than conventional spargers or surface entrainment aerators, according to the manufacturer. The aerator floats below the surface of a pond. Compressed air rises through the vertical unit moving water through the tube. Mechanical and electrical components are located remotely from the aeration unit so the device presents no hazard to bathers. Fish travel through the unit without harm, the company says, and the lack of moving parts cuts down on pollution from lubricants. Kenics Corp. **75**

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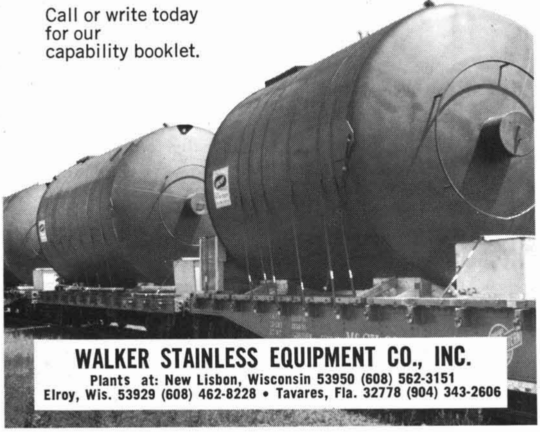

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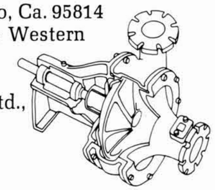

WEMCO
ENVIROTECH

Circle No. 21 on Readers' Service Card

Pollution equipment. New 20-page brochure features equipment utilized in air and water pollution studies. ACE Scientific Supply Co. **91**

Ecology bulletin. Four-page publication studies the prevention of water pollution. Includes details of instruments for testing soils for the disposal of radioactive wastes, measuring underground water depth, and studying geological and biological conditions of lakes, streams, harbors, and ponds. Soiltest, Inc. **92**

Solid waste handling. Typical solid waste processing operation is schematically described in Rex Bulletin 325-1070. This system features apron feeders, belt conveyors, bucket elevators, vibrating screens, and automatic weighing equipment. Rex Chainbelt, Inc. **93**

Waste water management. Twelve-page brochure discusses pollution control through waste water management. Provides details of Laicon's major areas of operation and offers diagrams and photographs of a typical installation. Laicon, Inc. **94**

Pollution solution. This 13-minute film describes benefits of utilizing underground, geological formations for disposal of chemical wastes. Covers ecology problems and the merits of considering the liquid waste disposal method. Fibercast Co. **95**

Waste water treatment. Twenty-four page technical booklet describes the UNOX System for treating waste water. Reviews history of previous investigations substituting oxygen for air and provides an explanation of the underlying basis of the system and its operation. Union Carbide Corp. **96**

Power generation problems. Booklet describes with diagrams and charts, power generation problems in the 1970's covering topics such as fossil fuel, nuclear power, steam and gas turbines, and the environment. Westinghouse Electric Corp. **97**

Plant effluent monitoring. Application bulletin E1.1207 describes monitoring dissolved oxygen in plant effluents. Features and benefits of typical D.O. probe and monitor systems are discussed. Leeds & Northrup Co. **98**

Waste water reclamation. New brochure describes Chemico's capabilities and total systems approach to waste disposal problems in the chemical processing, metallurgical, and petroleum industries. Also states basic approach to pollution problems allowing for economical regeneration, recovery, and recycling of effluents. Takes into account pollution codes, standards, and legislation. Chemico Corp. **99**

Filter aids. Description of diatomite, mining, and processing of diatomite ore, typical filtration systems, types of filters, fibers for filtration, and bulk handling of Celatom filter aids. Eagle-Picher Industries, Inc. **100**

Wet scrubber. Bulletin F-1703 describes the Hexadyne wet scrubber as an air pollution control device for foundry process, rock product, mining processes, and chemical or power plant operations. American Standard **101**

Demineralization. Description of instrumentation selection involved in a typical two-bed, ion-exchange demineralization system. Includes measurement and control of conductivity, pH, and monitoring sodium hydroxide and sulfuric acid. Leeds & Northrup Co. **102**

Fume scrubber. Bulletin A-125 describes fiber-glass fume scrubber designed for use in any installation to eliminate corrosive and harmful air

new literature

pollutants. Removes most types of industrial fumes, especially acids. Hartzell Propeller Fan Co. **103**

Water treatment supplies. Four-page catalog gives condensed specifications and identifies the full line catalog for detailed dimension data on the Tri-Clover line of stainless steel fluid control components for contaminant and corrosion resistant service. Ladish Co. **104**

Cooling towers. Booklets describe the design, construction, and functions of crossflow and counterflow cooling towers. Also, one booklet discusses the repair, modernization, and conversion of old or damaged towers. Ecodyne Corp. **105**

Phosphates. This brochure, "Phosphates, the Environment and You," informs the reader of the good and bad effects of phosphates. It particularly notes that eliminating phosphates from detergents will not solve the problem of eutrophication. FMC Corp. **106**

Cl and S determination. Applications bulletin explains use of sodium electrode in argentometric measurements and titrations. Useful to determine residual chlorides and sulfides in industrial water and waste water. Fisher Scientific Co. **107**

Monitoring algae growth. Publication describes monitoring algae growth in water pollution research. Reports a method for preparing specimens for electron microscopy and a microtechnique automating serial dilution antimicrobial susceptibility testing. American Instrument Co. **108**

Environmental consultants. Leaflet describes a check list of qualifications for environmental consultants. Useful for executives in industry, commerce, and government who are confronted with pollution problems. The Research Corp. **109**

New products brochures. One discusses sources of new products and the organizations that specialize in locating and developing new products for interested companies. The other specializes in refining patents and products for commercial application. TTA Information Services Co. **110**

Environ-lab. Bulleting describes and illustrates features of controlled environmental rooms. These have the ability to enable single or multiple environmental factors to be created and re-created to simulate natural growth conditions. Lab-Line Instruments **111**

Pollution surveys. Quarterly newsletter approaches the field of air pollution control by studying the physical and chemical properties and behavior of particulate contaminants. Characterizes the major and minor constituents of gases and their concentrations. Walter C. McCrone Assoc., Inc. **112**

Potomac, pollution and the people. Brochure provides information about the problems, advances, and hopes for the Potomac River. Government of the District of Columbia, Department of Human Resources, Health Services Administration, Washington, D.C. 20001 (Write direct)

Photolysis applications. A nine-page brochure covers such topics as photochemistry, triplet-triplet absorption studies, photosynthesis, visual pigment studies, electron transfer reactions, gas phase photochemistry as related to atmospheric pollution studies, and others. Xenon Corp., 39 Commercial St., Medford, Mass. 02155 (Write direct)

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bookshelf

Decision-Making in Air Pollution Control. George H. Hagevik. xiii + 217 pages. Praeger Publishers, 111 Fourth Ave., New York, N.Y. 10003. 1970. $15.00, hard cover.

Mr. Hagevik traces the history of air pollution control that has involved government participation on the federal, state, and local levels. He stresses the need for different approaches to control methods because of the diversity of the origins of air pollution. To meet the different technological, economic, and political considerations of each pollution problem, the author suggests the application of advanced economic methods of analysis and organization. ■

Opportunities in Environmental Careers. Odom Fanning. 250 pages. Vocational Guidance Manuals, 235 E. 45th St., New York, N.Y. 10017. 1971. $5.75, hard cover.

As the first comprehensive survey and analysis of this type, the book covers vocations in all five areas of environmental management—ecology, earth sciences, resources and recreation, environmental design including architecture, and environmental protection including public health and pollution control. The author gives specific advice to aid the high-school student in designing his curriculum for undergraduate and postgraduate studies. For each field of environment, the book defines terms, describes scope, lists activities, gives names and addresses of 175 leading colleges, generalizes earnings and working conditions, as well as listing other sources of information. ■

Our Natural Resources, 3rd ed. P.E. McNall, Harry B. Kircher. xviii + 296 pages. Interstate Printers & Publishers, Inc., 19–27 N. Jackson St., Danville, Ill. 61832. 1970. $4.95, hard cover.

Intelligent resource use and the principles of ecology are thoroughly discussed in this new edition. The book has been used as a text in schools throughout the nation and adopted in a number of states for statewide distribution. The new edition reflects and brings into sharper focus the problems of obtaining a better quality for our total environment and controlling the conflicts of interest which have led to its abuse. ■

America the Beautiful: A Collection of the Nation's Trashiest Humor. Anne Hamilton, Compiler, iii + 31 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1970. 35¢, paper.

"America the Beautiful" is depicted in a collection of cartoons that serve as a reminder that a crisis in solid waste management exists. The local incinerator and the city dump are targets for the humor of the social satirist. Cartoons from numerous publications throughout the country are reproduced. ■

Man's Impact on the Global Environment. xxii + 319 pages. MIT Press, 50 Ames St., Cambridge, Mass. 02142. 1970. $2.95, paper.

The interdisciplinary Study of Critical Environmental Problems presents an assessment of the existing state of scientific knowledge on global environmental problems. The book contains specific recommendations for action which reduce the harmful effects of pollution or would provide the information required to understand more adequately the impact of man on the global environment. If such information is not obtained, says the report, some critical environmental questions will remain unresolved, resulting in the inability to identify potential crises in enough time to avoid them and, possibly, to prevent irreversible global damage. ■

Environmental Radioactivity Symposium. John C. Clopton, Ed. vii + 272 pages. Department of Geography and Environmental Engineering, The Johns Hopkins University, Baltimore, Md. 21218. 1970. $5.00, paper.

The quest for information concerning the effects of environmental radiation upon biological systems prompted a symposium within which specialists in the radiological field could communicate and exchange ideas with students, faculty, and others of the Hopkins community. These proceedings discuss the discovery and rediscovery of information which would be of value to those who might make decisions, now or in the future, regarding environmental radiation levels. ■

Agenda for Survival. Harold W. Helfrich, Jr., Ed. xi + 234 pages. Yale University Press, 92A Yale Station, New Haven, Conn., 06520. 1971. $1.95, paper.

Derived from the two-year Yale School of Forestry symposium on "Issues in the Environmental Crises," this volume of papers is intended to serve as a reflective examination of our ecological problems. It contains the thoughts on the environmental issues of leading authorities from such diverse fields as the applied sciences, sociology, industry, conservation, urban design, architecture, law, politics, and public or personal opinions. ■

Selected References on Environmental Quality as It Relates to Health. Superintendent of Documents, Government Printing Office, Washington, D.C. 20402. 1971. $4.00.

All aspects of environmental pollution which concern health are covered in this new subject/author index. Each monthly issue contains citations to about 1000 pertinent articles selected from about 2200 of the world's biomedical journals. Among the 350 subject headings are acoustic trauma, automobile exhaust, detergents, dieldrin, industrial waste, noise, population density, and radioactive fallout. ■

Specialty Chemicals. 183 pages. American Chemical Society, Robert A. Fox, P.O. Box 607, New York, N.Y. 10017. 1970. $9.50, paper.

The American Chemical Society has published the papers presented at the September 1970 meeting of the Division of Chemical Marketing and Economics. One section, "Polymers in Water Management," covers water treatment topics. These subjects include applications of polymers to municipal water supply, phosphorus removal, oil recovery with synthetic polymers, polymers in water treatment, and ion-exchange systems for treating municipal and domestic water effluents. ■

Economics and the Environment. Allen V. Kneese, Robert U. Ayres, Ralph C. d'Arge. x + 120 pages. Resources for the Future, Inc., 1755 Mass. Ave., N.W., Washington, D.C. 20036. 1970. $2.50, paper.

This first monograph-length report deals with the management of residuals and of environmental quality. It represents an effort to break out of the traditional approach in pollution policy and research, which treats air, water, and solid waste problems as separate categories. "The external cost phenomena which economists have written much about are not isolated and somewhat freakish aberrations but are inherent in the production and consumption activities of modern economies," say the authors. ■

Physical and Engineering Aspects of Thermal Pollution. Frank L. Parker, Peter A. Krenkel. vii + 100 pages. Chemical Rubber Co., 18901 Cranwood Pkwy., Cleveland, Ohio 44128. 1970. $12.25, hard cover.

The major sources of thermal pollution, including central electric generating stations, are covered in detail in this volume. Coverage explores the rate of growth of cooling water requirements, the possibilities of improved efficiencies in electricity production, the limited availability of cooling water, and the mechanisms and means of heat dissipation. Two chapters are devoted to the effects of heated discharges upon the biota and hydrodynamics of the receiving water. ■

Films

Ground Water: The Hidden Reservoir. Ground Water Resources Institute, 221 N. LaSalle St., Chicago, Ill. 60601. 1970. $15.00.

America's groundwater supplies are discussed in this entertaining but fundamental educational film. The movie makes two major points—greater efforts must be made to return groundwater to the ground after use rather than draining it into the ocean; and that while the world is not running out of water, it must be managed cautiously and wisely. ■

Environmental Crisis: What the Individual Can Do. National Education Association Publications, Sales Section, 1201 Sixteenth St., N.W., Washington, D.C. 20036. 1970. $15.00.

Specific solutions for getting rid of traffic, water pollution, and nondegradable litter are presented in this color, sound filmstrip with 33-1/3 rpm record. The philosophy of ecology is given in a message from students to students for the upper-elementary to college-level viewer. ■

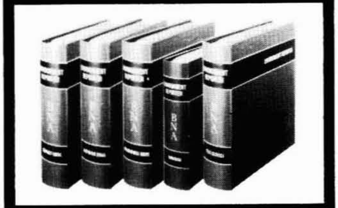
Games

Smog. Urban Systems, Inc., 1033 Mass. Ave., Cambridge, Mass. 02138. 1970. $10.00.

"Smog," the air pollution game, acquaints players with some of the complexities with which a local administrator must deal in controlling the quality of the air over his town. This game is very complex and takes much thought and effort. It should be useful in college-level courses in air pollution or those in air pollution control. ■

Dirty Water. Urban Systems, Inc., 1033 Mass. Ave., Cambridge, Mass. 02138. 1970. $10.00.

"Dirty Water" is a game that teaches people of all ages about ecology and water pollution. The purpose of the game is to acquaint the players with some of the complexities with which an administrator must deal in controlling water pollution to keep local bodies of water in a normal state of ecological balance. The players travel around the game board, by proxy of a token, collecting organisms to live in their "lakes." Pollution from neighboring lakes as well as overpopulation can adversely modify the life in the lake and the chance to win the game. The game is entertaining, easy to play, and can be enjoyed by all ages. ■



April 14-16
United States Jaycees
Fourth National Pollution Control Conference and Exposition
Detroit, Mich.

This conference covers all areas of environmental control—air, water, solid waste, noise control, and nuclear waste. Conference theme is "Environmental Control Answers and Alternatives." Contact: Aubrey LaFargue, General Chairman, 1107 S. Loop West, Houston, Tex. 77021

April 19-21
International Association for Great Lakes Research
14th Conference on Great Lakes Research
Toronto, Canada

Discussions will center around problems concerning the Great Lakes. Contact: Mrs. J. S. Seddon, Great Lakes Institute, University of Toronto, Toronto 5, Ont., Canada

April 19-21
Nine Engineering Societies
Third Annual Offshore Technology Conference & Exhibit
Houston, Tex.

Control of pollution, desalination, and corrosion are among topics listed. Contact: Paul Drummond, Manager, Conferences and Divisions, American Society of Mechanical Engineers, 345 E. 47th St., New York, N.Y. 10017

April 19-22
Ohio State University
International Symposium on Livestock Wastes
Columbus, Ohio

Program concerns livestock wastes: their treatment, disposal, pollution properties, and handling. Contact: International Symposium on Livestock Wastes, c/o The Center for Tomorrow, Ohio State University, Columbus, Ohio 43210

April 20
American Institute of Chemical Engineers
Eighth Annual Technical Meeting
Los Angeles, Calif.

"The Energy Crisis and Fuels Technology" theme includes relevant environmental problems and solutions. Write: Dan Chapel, Meeting Chairman, 2500 S. Atlantic Blvd., Fluor Corp., Los Angeles, Calif. 90022

April 22 and 23
Southern Interstate Nuclear Board, Tex. Radiation Advisory Board, and the Atomic Energy Commission
Innovative Applications of Radiation Conference
Dallas, Tex.

Includes major topic of "Environmental Effects." Write: Robert H. Gifford, Executive Director, Southern Interstate Nuclear Board, Suite 664, 800 Peachtree St., N.E., Atlanta, Ga. 30308

April 22 and 23
Univ. of Tennessee
Symposium on Air Pollution
Knoxville, Tenn.

Theme is "State of the Art of Air Pollution Control Techniques for Industrial Processes and Power Generation." Experts from education, industry, and government will discuss emission control, planning, and regulation from stationary sources. Fee: $25. Contact: Dr. W. A. Drewry, Dept. of Civil Engineering, Univ. of Tennessee, Knoxville, Tenn. 37916

April 25-30
Engineering Foundation of the United Engineering Trustees, Inc.
Engineering Foundation Conference
Pacific Grove, Calif.

Included in this conference is exploring the various environmental forces that affect quality. Also how the finished project serves society environmentally. Attendance is limited to 100 persons. Fee: $160. Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

April 26-30
Institute of Environmental Sciences
17th Annual Technical Meeting & Equipment Exposition
Los Angeles, Calif.

Theme is "Living in Our Environment." For details: T. W. H. Miller, IES, 940 E. Northwest Highway, Mt. Prospect, Ill. 60056

April 28
American Society of Mechanical Engineers
Air Pollution Symposium
Columbus, Ohio

Part of annual series to update technical men on pollution subjects of current importance. Fee: $15. For details: James A. Marshall, Dept. of Mechanical Engineering, Ohio State University, 206 W. 18th Ave., Columbus, Ohio 43210

meeting guide

April 30–May 1

Council of State Governments

Southern Conference Environmental Quality Committee

Atlanta, Ga.

Contact: Council of State Governments, Iron Works Pike, Lexington, Ky. 40505

May 3 and 4

School of Chemical Engineering at Oklahoma State University

Second Annual Conference on Synthetic Fuels from Coal—Gasification and Liquefaction

Stillwater, Okla.

Topics include economics and pollution aspects of the solvent refined coal process and the IGT gasification process. Contact: Monroe Kriegel, Director of Extension, College of Engineering, Oklahoma State Univ., Stillwater, Okla. 74074

May 3–5

Coordinating Research Council, Inc.

Automotive Air Pollution Research Symposium

Chicago, Ill.

Over 30 projects aim at the engineering aspects of vehicle emission control, atmospheric chemistry, and potential effects of automotive pollutants on health. Contact: Alan Zengel, Coordinating Research Council, Inc., 30 Rockefeller Plaza, New York, N.Y. 10020

May 3–7

International Council of Scientific Unions

International Symposium on Man-Made Lakes, Their Problems and Environmental Effects

Knoxville, Tenn.

Contact: Tennessee Valley Authority, c/o Scientific Committee on Water Research, Knoxville, Tenn. 37900

May 4–6

Purdue University

26th Purdue Industrial Waste Conference

Lafayette, Ind.

For details: Don E. Bloodgood, School of Civil Engineering, Purdue Univ., Lafayette, Ind. 47907

May 7

New York State Action for Clean Air Committee

Spring Meeting

Schenectady, N.Y.

Representatives of government and industry will discuss the problem of solid waste. Write: New York State Action for Clean Air Committee, 105 E. 22nd St., New York, N.Y. 10010

May 10–14

Solar Energy Society

1971 International Solar Energy Society Conference

Greenbelt, Md.

Papers presented on the use of solar energy in the environment—sewage disposal and water heating and purification. Contact: Bernard Goldberg, Smithsonian Radiation Biology Laboratory, 12441 Parklawn Dr., Rockville, Md. 20852

May 12 and 13

Univ. of North Dakota and U.S. Bureau of Mines

1971 Lignite Symposium

Bismarck, N.D.

Symposium on technology and utilization of fossil fuels. Features facets of environmental pollution. Contact: James L. Elder, 1971 Lignite Symposium, Box 8213, University Station, Grand Forks, N.D. 58201

May 17–21

University of Michigan

Seventh International Symposium on Remote Sensing of the Environment

Ann Arbor, Mich.

Measurement techniques to be presented include monitoring and control of environmental quality. Contact: Extension Service, Conference Dept., Univ. of Michigan, Ann Arbor, Mich. 48104

May 19–21

American Society for Quality Control

25th Annual Technical Conference

Chicago, Ill.

Includes session on environmental control. Write: Robert W. Shearman, Administrative Secretary, American Society for Quality Control, 161 Wisconsin Ave., Milwaukee, Wis. 53203

June 8–12

Pro Aqua-Pro Vita

International Exhibition for Sanitary Engineering, Water, Sewage, Refuse, Air, Noise

Basle, Switzerland

Information from: Secretary, Pro Aqua–Pro Vita, Post Box CH-4000, Basle 21, Switzerland

Courses

April 19–23

Manufacturing Chemists Assoc.

Advanced Seminar

New Orleans, La.

Instruction on chemical waste treatment for water pollution control. Fee: $210. Contact: Howard B. Brown, MCA, 1825 Connecticut Ave., N.W., Washington, D.C. 20009

April 26–28

Vanderbilt Univ.

Seminar on the Development of Design Criteria for Biological Waste Treatment

Nashville, Tenn.

Discusses biological treatment of municipal and industrial waste waters. Fee: $125. Write: W. Wesley Eckenfelder, Jr., Box 6222, Station B, Vanderbilt Univ., Nashville, Tenn. 37203

May 3–7

Water & Wastewater Technical School

Short Course on Pumps and Hydraulics

Neosho, Mo.

Will cover pump theory and acclimation including water and sludge pumps and others. Fee: $50. Contact: Robert J. Illidge, Water & Wastewater Technical School, Box 370, Neosho, Mo. 64850

May 5–7

Photo Data Institute

Short Course on Aerial Photographic Methods for Pollution Surveillance

Oshkosh, Wis.

More Information: Photo Data Institute, Box 529, Neenah, Wis. 54956

May 10–14

NUS Corp.

Advanced Fuel Management Workshop

Rockville, Md.

Covers spent fuel recovery. Fee: $650. Write: W. V. Macnabb or F. C. Duvall, NUS Corp., 4 Research Place, Rockville, Md. 20850

Special notice

1st ACS Environmental Improvement Exposition

In conjunction with the Washington, D.C. fall meeting and chemical exposition, September 12–17, 1971, the American Chemical Society will sponsor its first environmental improvement exposition. The exposition will feature products and services for pollution control and environmental management and will be held in the Sheraton Park Hotel. Exhibitors can obtain full details from: A. T. Winstead, Meetings and Expositions Office, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

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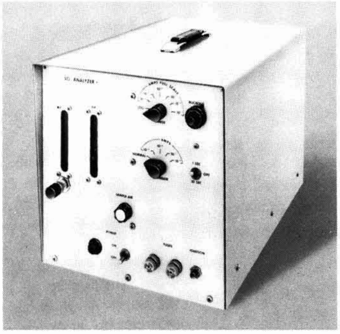

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