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contents

What is known about combustion of sulfur-containing fuels is reviewed, but much information is still lacking. In 1980, 42 million tons of SO_2 will be released into the atmosphere, up from the current annual release of 22 million tons. Five oxidative processes, the intermediary species of each, and the many interrelated factors that influence the presence of SO_2 in flue gases are summarized.

Simultaneous removal of SO_2 and particulates from combustion flue gas can be achieved with a simple shaft-filter-sorber. The shaft-filter-sorber consists of a bed of slowly falling alkalized alumina through which the pollutant-laden gas stream passes horizontally. Complete SO_2 and 99+% removal efficiencies were possible at gas mass velocities of 150 lb./hr. ft^3 and dust loadings in excess of 3 grains per s.c.f.

Common tree species including eucalyptus, willow, red oak, and mango have been found to release isoprene (an unsaturated hydrocarbon also found in automobile emissions) to the surrounding forest environment. Emitted under natural conditions from the intact, living foliage, isoprene has been found to be emitted from more than 30% of 230 plant species surveyed. At present, the biological fate and interactions of foliage emissions are poorly understood.

An improved field sampler for the determination of atmospheric concentrations of hydrogen sulfide at the 0.5–100 p.p.b. level uses a mercuric chloride-treated paper tape, rather than the conventional lead acetate-treated paper tape. The samples were stable over a 7-wk. period, and a single roll of the tape affords consecutive 2-hr. samples for a period of one month.

The nitric oxide (NO) content of automobile exhausts can be determined by a new analytical procedure. In the procedure, NO is converted to a mixture of nitrite (NO_2^-) and nitrate (NO_3^-) by treatment with aqueous potassium hydroxide. Then, simultaneously, the nitrite and nitrate contents are determined by a uv technique.

In various air pollution control systems, processing streams may take the form of jets of particulate suspensions. Knowledge of the transport and diffusion characteristics of these particles in these jets is useful for design of such control systems. Experiments were recorded for charged suspensions of glass and alumina particles; even a small charge markedly altered the radial position of jet boundary of the particulate phase.

Communications

The role of unsaturated hydrocarbons in photochemical air pollution studies is best explained in terms of atomic oxygen reactions. The excited atomic oxygen species is more important than a corresponding excited molecular oxygen species for such explanations and can be used to explain unsaturated hydrocarbons lost in the atmosphere.

Not associated with plant cellulose, selenium nevertheless has been found in paper and tobaccos. Selenium concentrations in cigarette and pipe tobaccos were 0.03–0.13 p.p.m.; in paper the values were usually less than 0.05 p.p.m., and in cigar tobacco the values were 0.33–1.01 p.p.m.

letters

Your article noted the lack of air pollution controls. By far the most important item of pollution control (in any disposal system) is operator technique. This is gained by experience, which the Goodfellow personnel is adding to constantly. Also, detailed knowledge of the nature of the wastes being handled is a most important aspect of pollution control. All wastes being accepted by the Goodfellow plant are properly identified before they arrive for disposal.

We are very proud of the Goodfellow facility, and the industries it serves are very thankful for its existence. We are confident that the pollution control agencies in Ontario are equally thankful for an acceptable alternative to indiscriminate dumping of industrial wastes.

W. K. Lombard
Vice-president and general manager
Trecan, Ltd.
Mississauga, Ontario

Pesticide views draw fire

DEAR SIR:

Parke C. Brinkley's Viewpoint in your May issue, page 369 ("Pesticides are important as antipollutants") is generally ill-informed and illogical. For example, the runaway rat populations that he talks of are usually the *result* of human pollution; the problematic "green scum" he mentions is usually the *result* of human pollution, and so forth. But the pervading fallacy in his discussion of pollution is found in the first paragraph: Pollution is anything that makes "the environment unsuited to your existence and comfort." This puts man's pleasure at the top of the list of priorities when attempting to coexist with our environment. This, I believe, is ultimately the cause of all our pollution problems. Furthermore, it subjects nature to man's haphazard, Madison Avenue influenced value system, e.g., grass without dandelions is better than grass with.

Eventually, the real value of pesticides and their safe and constructive use will be determined. Hopefully, Mr. Brinkley will not be influential in this evaluation.

Larry Vanderhoef
Dept. of Plant Pathology
Univ. of Wisconsin
Madison, Wis. 53706

DEAR SIR:

I cannot support the viewpoint expressed by Parke C. Brinkley (ES&T, May 1970, p. 369) that "pesticides are important as antipollutants." It is indeed disheartening that such a leading figure as Mr. Parke C. Brinkley should advocate the indiscriminate and loose application of the word "pollution" to such things as mice and rats, insects, weeds, etc., and to foodborne *Salmonella*, when the more appropriate terms are "infestation" and "contamination."

I do not dispute that pesticides have a continuing role in the control of pests and disease vectors. But to go to the extent of calling pesticides "antipollutants" is clearly a step backward in your efforts to support the management of environmental quality.

I am disappointed that ES&T has found it acceptable not only to publish Mr. Brinkley's article but also, by doing so, to imply that his viewpoint should be promoted.

S. K. Krishnaswami
Department of National Health and Welfare
Ottawa 3, Ontario

Rebuttal on a reevaluation

DEAR SIR:

A letter to the Editor in your June issue, p. 453, "Air pollution sources reevaluated," closes with the thought that the new methods discussed "are not the final answer to this delicate problem." This is reassuring, since the methods leave a lot to be desired from the standpoints of plausibility and general application.

We agree with the statement that "simple statistics often used do not really present a true picture." But we feel strongly that the authors (Robert F. Sawyer and Laurence S. Caretto of the University of California) have fallen into the trap of using a very simplified weighting procedure to try to put a complicated picture into perspective. They also are guilty of using ancient data (1965) and, worse, zeroing in on specific regions to use national figures which are not now— and never were—applicable in those regions.

For example, the authors conclude that "A Southern California Edison Co. statement that only 1% of the Los Angeles area air pollution comes from power plants is grossly understated." This is a serious misquote.

Our company has always presented the 1% figure (based, incidentally, on official L.A. County Air Pollution Control District data) in the context of total tonnage of air pollutants emitted in the county. Use of 1% as related to the terms "air pollution" or "smog" in the Los Angeles area is improper.

Moreover, by using 1965 national figures, the authors ignore three important factors: (1) California generating plants have customarily used cleaner-burning gas and oil as their fuels, unlike plants elsewhere which rely largely on coal. (2) Since 1968, our company has been supplementing natural gas fuel with low sulfur, low ash oil imported from Indonesia. This switchover prompted the APCD to report that air pollution complaints about power plants "ceased abruptly" in the winter of 1968–69. (3) A recent series of research breakthroughs have reduced SCE emissions of nitrogen oxides from 14% to 8% of the total in the Los Angeles Basin.

We agree with the authors that the "uncertainties in (their) weighting factors remain high," but would also like to point out that some of the ambient air standards were not applied properly to arrive at their weighting factors. For example, the standards of 5.25 p.p.m. for NO_x, 0.04 p.p.m. for SO_2, and 20 p.p.m. for CO were applied without regard to the fact that the 0.25 p.p.m. is really for NO_2, not NO_x (it would be higher for NO_x), and without recognition that the standards apply to differing time periods of 1 hour, 24 hours, and 8 hours, respectively.

Many air pollution authorities agree with our conviction that it is the effect of a pollutant source at ground level that really counts and is of prime importance. Thus, a given amount of NO_x emitted from a stack hundreds of feet in the air should be weighted far less than the same amount emitted, along with hydrocarbons, from the tail pipes of automobiles at ground level. The authors gave them equal weight, however, and we believe this is another serious error.

Because of the importance and complexity of the subject matter, I believe it would have been appropriate to accompany the Sawyer–Caretto letter with competent rebuttal.

William R. Walker
Southern California Edison Co.
Los Angeles, Calif. 90053

Pollution business in the doldrums

Where's the huge market we've been hearing about?
All the signs indicate that it's just around the corner

Pollution control—said a respected (and expensive) investment advisory service back in January—"is an idea whose time has come." To judge from the performance of the so-called pollution control stocks in the market since that time, its time has come and gone. During a period (January–July) in which the Dow Jones industrial average slipped 14%, the stocks of many companies who purport to be in the pollution business have lost 50% or more. To be sure, some of the enthusiasm for such stocks always was based on factors more illusory than real: euphoria regarding President Nixon's January environmental message; infatuation with companies built around the appeal of fashionable words such as "ecological." But, as we have suggested on this page before, there are good reasons why knowledgeable firms should be able to make money through pollution control. Chief among these is industry's (grudging) willingness to pay for inexpensive technical solutions to its pollution problems.

Unfortunately, something seems to have gone wrong, at least for the moment. The widely made assumption that talk necessarily leads to financial commitment turns out to have been partly incorrect. Sales of pollution control equipment seem to bolster the point. The Industrial Gas Cleaning Institute—whose member companies make 75% of the air pollution control equipment sold in the U.S.—reports that sales in 1969 were only 2% higher than in 1968. First quarter earnings of many equipment companies give no reason to expect that 1970 will be much better. Yet cleanup has to come, and the bill will inevitably run to billions of dollars, much of it presumably going to companies in the pollution control business.

Why, one may ask, is reality so far removed from the expectations of investors (admittedly a group not noted for being overly patient)? Well, first of all there is the scarcity of money, and its expense when available for loan. Then, there is the ever-present reluctance to spend on an inherently profitless purpose in a time when profit margins are being squeezed. Neither of these reasons would mean anything, of course, if polluters were *forced* to spend to abate pollution. Whether lack of coercion is due more to the absence of laws or to nonenforcement of laws on the books is a matter for some debate, but the fact remains that it is still possible in most places in the U.S. to pollute without being criminally prosecuted or jailed. At the same time, there is general acceptance in industry and among members of the public of the idea that laws will become more numerous and more strictly enforced than in the past. If this idea is sound—and there is every reason to believe that it is—then the market for pollution control equipment and services is bound to explode. Everyone expects the explosion soon. The big question is how soon?

Certainly, more firms are entering the pollution business: this year's ES&T Pollution Control Directory, now in preparation for publication with the November issue, will list 70% more companies than last year. And, projections of the market continue to be remarkably bullish. Two stories in this issue, for instance, deal with a possible $500 million market for instruments that monitor air pollutants and a potential industrial market twice as large for desalination process technology.

It therefore appears that, while spending for pollution control continues at what can only be described as a sober pace, potential demand (and certainly potential supply) is piling up. In order to give readers a better idea of how demand and supply are running, ES&T will, starting this month, expand its listing of expenditures for pollution control and of business developments in the industry (see Industry Trends, page 688). These items have previously been covered to a small extent in Environmental Currents. We expect this column to grow in size as paper projections are transformed into solid business for the pollution control industry and a cleaner environment for everyone.

D. H. Michael Bowen

"THIS DUST HAS MADE MY EYES SORE AGAIN."

He got it in the eye.

And so did management.

He loses time and wages. Management loses a good man and production. Nobody wins when both sides lose. The profit-and-loss statement doesn't win either.

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viewpoint

Barry Commoner
Washington University, St. Louis, Mo.

Present benefits and future risks

The nation has suddenly awakened to the fact that we are in a grim and potentially fatal environmental crisis. The enormous power of modern technology is stressing the environment, breaking vital links in the web of biological processes that sustain the ecological system in which we live. With this power we have acquired a new responsibility: to be prudent and conservative stewards of the thin global skin that sustains us and all who will follow us on this planet. In response, citizens are demanding new and more stringent rules to govern the balance between the benefits and risks of new technology.

Public opinion has already defined limits to the risks which are acceptable in exchange for the benefits from a wide range of activities: driving a car, traveling in a train or an aircraft, skiing, working in an industrial plant or living near it. These are personal, voluntary acts. Other benefit–risk issues relate to large-scale social enterprises in which the risks are involuntary. Chauncey Starr (*Science* **165,** 1232, 1969) has evaluated the quantitative balance between the benefits and risks associated with such activities which has in the past been accepted by the general public. A striking result of his study is that for activities of equal benefit the public will accept a risk about 10,000 times higher when the activity is voluntary rather than involuntary.

Recent developments attest to a new appreciation, on the part of the public, for the social, aesthetic, and moral value of an unpolluted environment. In response to public demand, pollution standards which have long been accepted without complaint have been made considerably more rigorous.

One explanation for this change is suggested by the ten thousandfold difference between the acceptable benefit–risk ratios of voluntary and involuntary activities. This reflects a more stringent public morality when action of some members of society impose a risk on others, who are given no choice in the matter. The new assaults on the environment considerably intensify this moral factor. I believe that the public has now become aware that environmental pollutants represent an assault by the present generation not merely on involuntary *living* victims—who have some recourse, however difficult—but on generations not yet born, and thus defenseless.

It is proper and fitting that acceptable levels of pollution should be established by public mores. While evaluation of the benefits to be derived from an insecticide or a power plant and an estimation of the resultant environmental hazards require scientific analysis, the choice of the balance between benefit and risk does not. There is no way for science to determine that it is better to suffer a high rate of emphysema than it is to raise the taxes required for a pollution-free system of urban transportation. This is a social, political, and moral judgment. Like all such judgments, it belongs, in a democracy, not in the hands of experts, but in the hands of the people.

But how can the ordinary citizen exercise his judgment if he does not understand the technical facts that determine benefit and risk? This creates a new task for the scientific community: to provide, freely to the public, in understandable form, the scientific evidence relevant to the benefits of new technology and their environmental risks.

Good beginnings have been made to meet this responsibility. For example, committees of scientists affiliated with the Scientists' Institute for Public Information have already made important contributions to public information about pollution problems: in Minneapolis and New York on reactor siting; in Rochester on water pollution; in Colorado on the hazards of nuclear operations; in California on pesticides; in St. Louis on the whole range of environmental issues through the magazine *Environment*. But this is only a small start. If this nation is to solve its massive environmental problems by democratic means, every citizen must be informed about the relevant benefits and hazards of the technological age. It is time for the entire community of scientists to take up the task of environmental information.
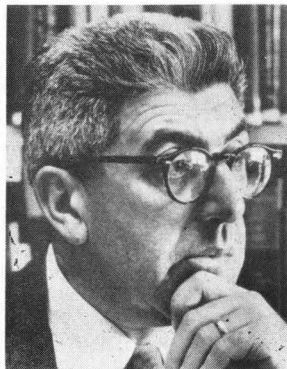
Barry Commoner is Director, Center for the Biology of Natural Systems, Washington University

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for better environment
Clayton

environmental currents

Nixon announces new pollution control agency

The Environmental Protection Agency (EPA), an independent agency within the executive branch, brings together the major federal pollution control programs (*see box*) which are currently funded at the $1.4 billion level in fiscal year 1971 and involve 5650 persons. Standard and enforcement procedure for pollution control under existing laws remain the same and are a principal EPA concern, but one EPA priority is to delineate further needs for pollution control legislative authority. EPA reorganization becomes final within 60 calendar days, unless vetoed by a majority vote of either house of Congress, and effective within another 60 days. At the same time, the National Oceanic and Atmospheric Administration (NOAA), an independent agency within the Department of Commerce, was also announced.

NAPCA: test procedure—manpower needs—auto race

The new test procedure for auto emissions which will be used for prototype testing of 1972 automobiles was published last month; comments from industry are due within 60 days. The new procedure measures total exhaust volume of emissions (ES&T, July 1969, page 625) and would reflect a tightening of controls for the automobile manufacturers. In its manpower and training needs for air pollution control, NAPCA finds that the manpower for state and local agencies must increase from 2300 in 1969 to 8000 in 1974 and for NAPCA positions must increase from 1000 to 2900; The low emissions, cross-country, automobile race (from Cambridge, Mass., to Pasadena, Calif.) is gearing up; 70 entries will head West on August 24 after qualification including emission checks.

Interior's water regulations become effective

Regulations for the federal construction grants program became effective last month (ES&T, May 1970, page 371). They require • Comprehensive river basin-wide programs. • No new federal grants for systems designed to treat industrial wastes only. • System of cost recovery must be implemented wherever some industrial wastes are to be treated in a new plant built with federal aid. • State water pollution control agencies must inspect new facilities for efficiency and economy. FWQA also announced: • Field testing of the self-degrading DDT by Aerojet General (El Monte, Calif.). • Feasibility study of locating a 1000-megawatt nuclear electric power plant underwater offshore by General Dynamics (Groton, Conn.).

Commerce advisory board reports on lead additives

Regulation of fuel additives by the federal government for nationwide availability of low-leaded fuel by 1972 and general availability of unleaded grade of gasoline by the middle of 1974 are the principal recommendations of the Commercial Technical Advisory Board (CTAB) on Automotive Fuels and Air Pollution, the nine-man panel chartered in March (ES&T, May 1970, page 371). In its preliminary report, CTAB does not recommend a ban on leaded gas after July 1, 1974 and leaves many options open on ways to meet 1975 auto emission standards. CTAB's final report on the broader issue of changes in fuel composition and additives is due the first quarter of 1971. Another CTAB report on noise is due to be released in the fall.

STATES Financing needs for water pollution abatement

For the next six years, the combined needs for water pollution controls
in the U.S. will total $33–37 million, according to a recent report prepared
by the National League of Cities and the U.S. Conference of Mayors.
Based on a survey of more than one thousand areas, which serve nearly
90 million persons, the findings endorse the funding program of $2.5
billion a year for five years for the construction of municipal treatment
facilities—the figure specified in Sen. Edmund S. Muskie's (D.-Me.)
pending proposal, S. 3687. The administration is recommending a four-year
authorization totaling $4 billion (federal share) of a $10 billion
construction program. Under existing law, a funding of $1.25 billion
is authorized for fiscal year 1971.

States indicate ire over air quality control regions

In separate events, Missouri, New York, and other state air pollution
control officials are unhappy with the designation of regions within their
states. Some would like to see their state designated as a single air
pollution control region. For example, Gov. Nelson A. Rockefeller has
requested that New York be designated one region. Two interstate and
one intrastate regions have been designated for N.Y., but federal
boundaries do not agree with those found by the N.Y. officials. The
Missouri Air Conservation Commission (MACC) voted to request the
federal authorities to designate outstate Missouri a single region, rather
than the two proposed by HEW.

N.Y.'s pure waters program—four years of progress

"New York's progress (in water pollution abatement) . . . is unmatched
anywhere else in the nation," says Gov. Nelson A. Rockefeller. The progress
is detailed in a recent report. By the end of last year, 117 municipal
treatment plants had been completed at a cost of $130 million; an additional
26 plants costing $33 million were completed during the first five months
of 1970. To date, 252 projects have been approved by the state a total cost
of nearly $1.6 billion; pure waters' funds amounted to 53.5% of the
total cost. By 1972, 546 projects are expected to be underway at an estimated
total cost of $3.1 billion. Formerly, in the N.Y. health department, the
divisions of pure waters became part of the Department of Environmental
Conservation on the first of July.

Gov. Nelson Rockefeller

Florida voters will pass on financing issue

A program of state loans for municipal and county sewage
treatment plants face Florida voters in its upcoming November election.
If ratified by the voters, the program permits issuance of $100 million
in bonds each year for the construction of water pollution abatement
facilities. Placing the full faith and credit of the state behind the bonds
will ensure a lower overall interest rate, making it unnecessary for
local governments to go into the bond market. A dozen other environmental
bills have been signed by Gov. Claude R. Kirk, Jr. These include:
• Requirement for a minimum of secondary treatment on all new
ocean outfalls and disposal well systems used for sewage disposal by
July 1; existing systems have till January 1974 to comply. • Fines for
violation of pollution law increased from $1000–5000 per violation.

environmental currents

TECHNOLOGY

Pure oxygen aeration gets major test in New York City

New York will take a look at pure oxygen aeration as a means of updating some of its existing sewage treatment plants with a $1.5 million grant from FWQA to which the city will add $900,000 for a $2^{1}/_{2}$ year study. One of fifteen 20-m.g.d. aeration tanks at the Newton Creek treatment plant in Brooklyn will be adapted to Union Carbide's Unox process; the study will also consider the effectiveness of alum addition for phosphate removal. City spokesmen hope the process will find an economical way of achieving 90% BOD removal at the Newton Creek where present removal is only about 40%. Oxygen will be supplied from an on-site generating plant.

BS&B coal combustion process
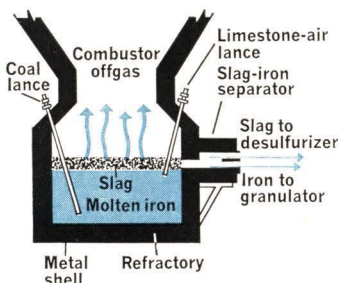
Coal combustion in molten iron avoids SO_2 formation

A radically new combustion process has been announced by Black, Sivalls & Bryson, a subsidiary of International Systems & Controls, for eliminating SO_2 emissions from power boilers. Pulverized coal is injected pneumatically into a mass of molten iron to be partially burned to carbon monoxide. Elemental sulfur is liberated, binds with the iron, and floats to the surface to form a slag with limestone, which is also injected into the iron along with the combustion air. Elemental sulfur can be recovered from the slag which is continuously drawn off. Offgases from the combustor are completely oxidized with secondary air above the combustor and proceed to a conventional boiler for steam production.

Landfills seen as threat to groundwater supplies

"The potential pollution of groundwaters by the products of sanitary landfill refuse decomposition is a problem faced by many large communities in California," J. J. Coe told the American Water Works Association meeting in Washington, D.C. Coe, chief of planning for water resources in California, explained three mechanisms for contamination: organic material leaching from the landfill to deplete oxygen and create anerobic conditions; inorganic leachates, usually permanent, increase total hardness and alkalinity; and CO_2 diffusion, which results in turbidity, color, and odor. Coe says California is considering classifying all refuse as to its pollution potential, and rating the landfill sites themselves as to degree of protection for groundwater. Where adequate natural protection doesn't exist, artificial barriers such as plastic membranes or asphalt lining would be used.

High temperature municipal incinerator slated for N.Y.

Construction has begun on a unique high temperature incinerator near Buffalo in Erie County, N.Y. The incinerator concept, developed by Torrax Systems, Inc., features a gasifier which is fed at the bottom with high temperature combustion air, preheated up to 2000° F., and at the top with untreated and unsorted refuse. The high temperature gases permeating up through the refuse charge decompose organic material near the top to form combustible gases, which are drawn off and burned in separate ignition chamber. Slow burning and noncombustible materials travel down the gasifier and are converted by 2600–3000° F. temperatures at the bottom into a liquid slag and a mixture of molten materials. These are drawn off and fed to a quench tank.

environmental currents

Stack gas treatment processes go commercial

Two SO_2 control processes for power plant boilers are slated for full commercial testing. The **Chemico-Basic Process** for adsorption by magnesium oxide will be installed at a 150-megawatt oil burning station of Boston Edison, with an expected reduction of 90% in SO_2 emissions. Spent adsorbent will be shipped to **Essex Chemical Corp.** in Clifton, N.J., for recovery of up to 17 tons of sulfur daily as sulfuric acid. And Monsanto's catalytic oxidation process for SO_2 removal will be installed at the Wood River, Ill., plant of Illinois Power Co., if the Illinois Commerce Commission approves the project. Wood River is a 100 Mw coal burning plant. About half of the installation costs of each unit will be borne by the National Air Pollution Control Administration.

Industry, universities represented on CEQ advisory panel

The Council on Environmental Quality has set up an 8-member advisory committee to assist in development of nonpolluting auto engines by 1975. CEQ chairman Russell Train explained that the role of the committee will be to guide development of alternative power sources should the auto industry fail to meet its announced goals of cleaning up internal combustion engines to meet proposed post-1975 standards. The development will take the form of: a series of R&D grants, some of which have already been made, by NAPCA's advanced automotive power system program to bring a number of alternative power sources through the development of second generation hardware suitable for mass production by 1975; and stimulation of independent industry R&D through an incentive plan that could lead to major purchases of certified low-emission vehicles by the General Services Administration.

Gillette to study phosphate-free detergent

The **Gillette Co. Research Institute** (Rockville, Md.), has been awarded a $344,000 contract by the Federal Water Quality Administration for the development of phosphate-free laundry detergents. In making the announcement, the Department of the Interior also disclosed that the Academy of Natural Sciences (Philadelphia, Pa.), has been selected as a subcontractor to assist in evaluation of the formulations. Carl Klein, assistant secretary for water quality and research, explained Gillette, will synthesize a number of detergents—each containing a different phosphate substitute—and determine their biodegradability, laundering characteristics, and potential for stimulating algae growth. The Academy will perform toxicity studies on promising formulations.

Kodak offers data on mercury analysis and dangers

With the threat of mercury pollution becoming increasingly serious, **Eastman Kodak** is making available a bibliography of internal technical know-how on mercury analysis and control it has developed over the past 30 years. Don H. Anderson, director of Kodak's industrial laboratory says, "the techniques we use in our lab are between ten and a hundred times more sensitive than methods in general use," and added "we can provide several publications written from our experience showing how to collect good samples, how to put together a good analyzer from components available in most labs, and ways to correct for substances that could interfere with the analysis for mercury. Requests for these publications will be handled through Kodak Corp.'s Information Department.
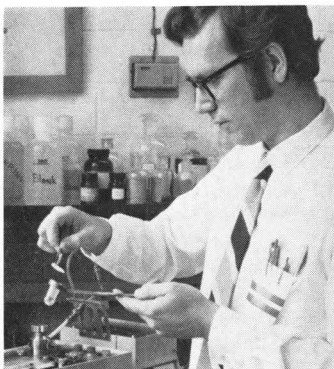
Testing for mercury

Converting solid wastes to electricity

*Combustion Power's CPU-400 concept is further along
than any other innovative solid waste disposal program*
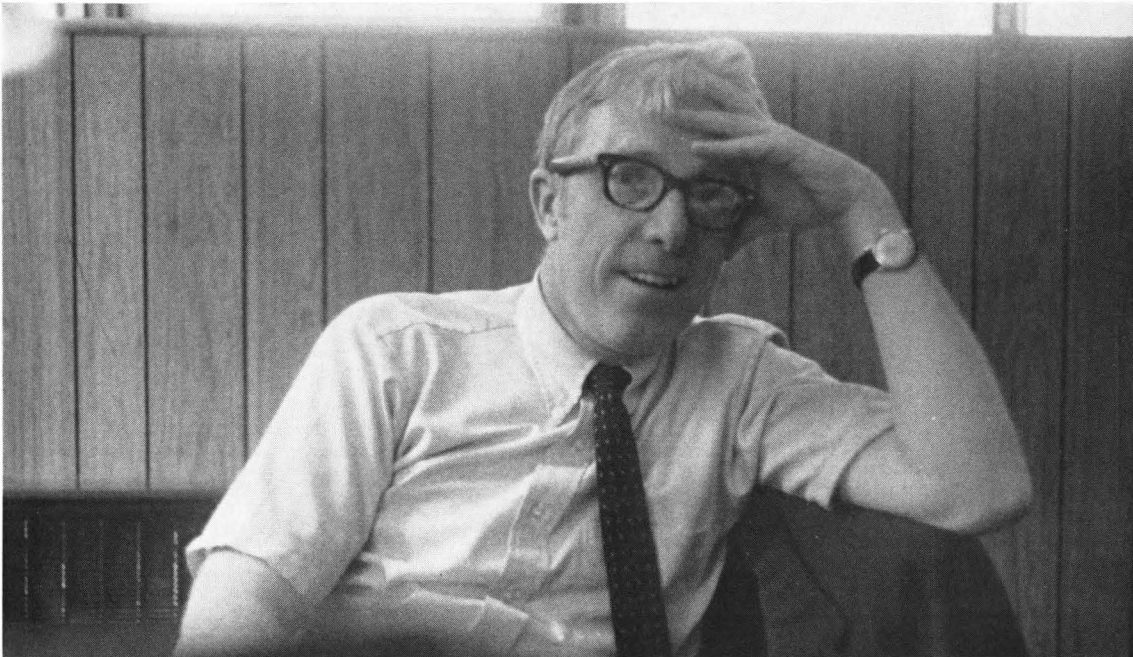
President. *Richard D. Smith notes that the U.S. should leapfrog European incinerator technology*

What would be the optimum design for a packaged solid waste disposal plant which might serve as a prototype for deployment throughout the trash laden areas in the U.S.? Faced with this problem, but given the latitude, freedom of selection, and financial backing of the Department of Health, Education, and Welfare (HEW), Combustion Power Co., Inc. (Menlo Park, Calif.), has hit upon an attractive concept, embodied in its CPU-400 unit. The unit consumes 400 tons per day of solid waste—the amount produced by 160,000 persons—to produce 15,000 kilowatts of electricity, approximately 5–10% of the total power consumed by that number of people. In the jargon of recycle and reuse, the energy value

of solid waste is used to produce electricity, leaving other valuables to be recycled.

Recognizing that the transportation cost is 75% of the trash bill, actual disposal accounting for the remaining 25%, the Combustion Power (CP) team reasoned that by optimizing the system, it could come up with a design in the forefront of technology. And, indeed, this is precisely what it has done. Now the goal of the joint CP/HEW effort is to demonstrate a standard unit for the disposal of solid wastes that can be put in place anywhere in the U.S., one year after the order is placed.

The CP team, a group of highly talented personnel who formerly

worked in the nation's defense program, is out of the rocket business. "I formerly worked for United Aircraft (Sunnyvale, Calif.), on the 120-inch solid rockets for the Titan III intercontinental ballistic missile," says Richard D. Smith president of Combustion Power. "It's a conservative guess, but when the CP team started on this problem, the solid waste disposal business probably had not had any new technology applied to it in the last fifty years.

"A number of new companies have entered the field in the last year or so," Smith elaborates. "Of the various dramatically new concepts that are being considered for solid waste disposal, the CPU-400 program is further

along simply because it started earlier. We are literally three years into the program."

Unit operation

Using a systems approach and weighing input-output factors, the CP team decided that nonhomogenous trash would be:

• Shredded to an homogeneous mass of uniform density. No separation or sorting would be accomplished prior to shredding.
• Passed through an air classification system to remove metals, glass, and rocks. After separation, the latter would be recycled.
• Dried and used as a source of energy. The organic portion has a caloric value one-third of high grade coal.
• Combusted in a fluid bed of sand at 1650° F., four times the amount of air necessary for complete combustion of the solid waste would be used. Use of the fluid bed provides complete combustion of solid wastes and air pollution requirements are met by cleaning high pressure gases upstream of the turbine.

Investigating ways to use waste heat (the heat not used to produce electric power), CP hit upon the idea of providing options which could be selected by the city or region based on its needs and geographic location. The options include conversion to steam, water desalination, and sewage sludge incineration. For example, a town in the North might be interested in the steam generation option for heat during the winter months. On the other hand, an arid region in the Southwest might choose the water desalination option, and so on. Because of the gas turbine, various options become possible.

The most expensive single component of the CPU-400 is the gas turbine. A number of 15,000-kilowatt gas turbines are in regular service; hundreds of such units have been produced and are generating electric power all over the world.

In addition to the above options, a vacuum collection system could be installed as yet another capability in a downtown office building, and the CPU-400 unit itself could be placed in the basement of an office building in a high density area. The compressor on the CPU-400 turbine is powerful enough to collect 400 tons of solid waste from the surrounding urban environment in approximately two hours.

Simple burning of the waste by incineration is wasteful and expensive. About 80% of domestic refuse consists of paper and plastics, the rest is minerals, metals, and glass. The CPU-400 uses the organic portion of the waste for heat and energy; the metals, glass, and heavy inerts can be recycled. Some materials are in short supply and require recycling; others, such as pulp and paper products and plastics, are more plentiful and can be used, according to a study by the national Library of Congress. Indeed, CPU-400 uses this plentiful supply of organic materials and converts it into electric power, a commodity in short supply.

Approaches

The big problem facing federal, state, and local decision-makers is a choice between constructing either large regional incinerators—in essence following European technology—or a much smaller packaged unit based on U.S. technology that can be dispersed within the region to minimize transportation costs. "Rather than copy them, we should leapfrog their technology and use the vast storehouse of knowledge from our space and defense work to put us squarely in the lead," Smith says. "The heat release

CPU-400 Input-Output plus options
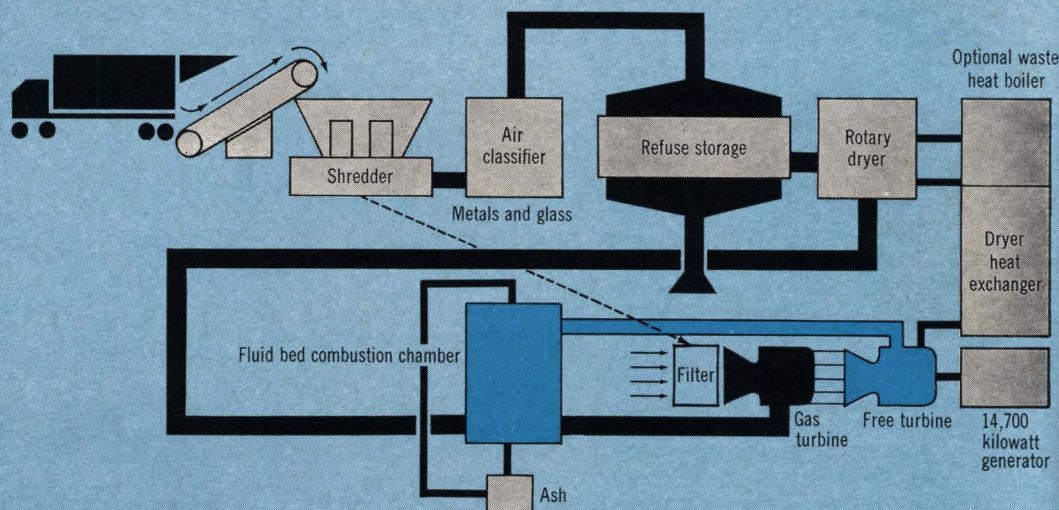
rate in the combustors of the CPU-400 will be more than 30 times that in the European incinerator."

Elements of CPU technology were already on hand. Those that required development have been tested and verified in subscale experiments. Now, the CP team is faced with the requirement to assemble the critical mass of these elements into a one-tenth scale pilot plant. At a later time, the first prototype unit will be constructed and demonstrated.

In brief, a fluid bed burning shredded refuse at elevated pressure is feasible, and the California firm now has design numbers on the system. The critical components are the fluid bed and the particulate collectors which are used to remove solid particles from the gas stream at 1700° F. before it enters the gas turbine.

"Some of the critical components in the design had to be verified by actual experimentation," Smith explains. "One experiment was the actual burning of refuse in a fluid bed combustor at high pressure (100 p.s.i.a.), work which was performed under subcontract by the Marquardt Corp. (Van Nuys, Calif.), a manufacturer of ramjets.

"Another experiment evaluated the effectiveness of three different types of particle collectors," Smith continues. "These included an inertial separator of the Donaldson Co. (Minneapolis, Minn.); a Research-Cottrell electrostatic precipitator operating at 1650° F., and a ceramic-type fabric filter. All three were tested in reasonable scale so that the CP team could simulate as precisely as possible the operating conditions of the CPU-400."

Pilot plant

"We began the first phase of the pilot plant earlier this year," Smith says. "Its fluid bed will be 8 feet in diameter. We have to design for uniform distribution of the bed over the entire 8 feet. Although the experimental bed was only 1 foot in diameter, the full-scale CPU-400 will have two beds, each being 12 feet square."

The pilot plant phase of the program will take about 1½ years. "With optimum funding, it will be complete by September 1971," CP's president says. "To date, approximately $2 million has been spent in this development. In all, $19.5 million is the funding that is needed to demonstrate the CPU-400 concept; that milestone will be reached sometime in 1974."

Although the pilot plant is being assembled in Menlo Park at present, the location of the full-scale prototype demonstration CPU-400 is a sensitive, unsettled decision yet to be made. That decision rests with HEW and more specifically with its Bureau of Solid Waste Management (ES&T, August 1969, page 705).

Potential

CPU is not limited to domestic application. Not only will it dispose of domestic wastes, but also industrial wastes. "We think of industrial waste as part of the waste," Smith says. "A smaller unit, based on the one-tenth scale pilot plant might be desirable for industrial disposal only."

Manpower requirements for operation the CPU-400 have been kept to an absolute minimum. No longer will human labor be required for the segregation and handling of solid wastes. The reduction in manpower is another plus for the system.

The names and numbers of cities and towns where CPU-400's could be put to good use are practically endless. These include towns having a population of 160,000 or more, as well as large urban metropolitan areas such as New York, San Francisco, and the like, where several units could be used advantageously.

Certainly, there is no best way of handling domestic trash. Landfill sites are slowly disappearing along with the rationale that landfills are the preferred disposal method. On a disposal cost argument alone, CPU-400 wins out; solid waste disposal by the CPU-400 would cost $1.20 per ton. In comparison, landfill operation costs $2.00 and incineration, $7.00 per ton.

CPU-400 stands out as the leading development for the disposal of domestic and industrial solid wastes. Its flexibility, adaptability, and choice of options make it a real contender for the solid waste disposal facility of the future. If funds for federal grants such as those in the pending federal legislation, become available for such construction, CPU obviously merits consideration.

Late in June, the House passed its version of the Resource Recovery Act of 1970 (H.R. 11833). The House approved authorizations of $83 million for fiscal year 1971, $152 million for 1972, and $216 million for 1973. The Senate approved $309.5 million over a 4-year period.
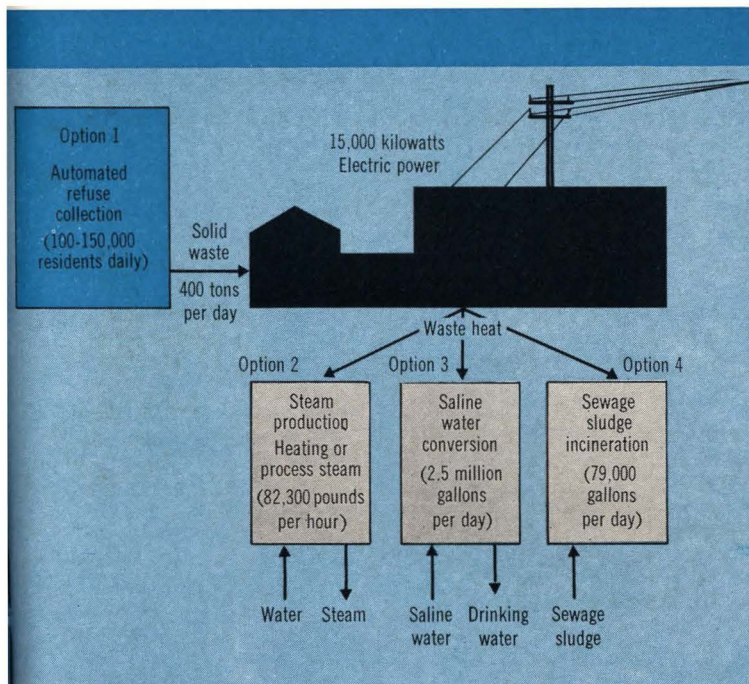
Desalters eye industrial markets

A potential market of over $1 billion for desalination equipment sales to industry is foreseen by an economist at the Office of Saline Water (osw). Speaking to attendees of a conference of the American Water Works Association in Washington, D.C., Eric D. Bovet, economic adviser to osw, spelled out reasons why he believes that equipment and processes originally developed for desalination of seawater and brackish waters can more than pay their way in the treatment of many industrial wastes.

Bovet's optimism is based in part on the results of a study undertaken for osw by Aqua-Chem, Inc. (Waukesha, Wis.). Aqua-Chem was asked to identify industries in which liquid wastes met two simple requirements:

• A by-product must be recoverable from the waste through one or more desalination processes.

• The commercial value of the by-product must equal or exceed the processing cost. Desalination has, in the past, been aimed almost entirely at the production of potable water, and the aim of osw is partly to expand horizons for the whole range of processes developed for that purpose, many with the assistance of osw funds.

Prime markets

The Aqua-Chem study identified six large potential markets for desalina-tion technology in industries where wastes meet the above requirements.

In **the cheese industry,** the major barrier to reclamation of the whey produced as a by-product is its salt content (about 1%). According to the Aqua-Chem study, a combination of reverse osmosis and electrodialysis process steps could produce a protein supplement grade of whey that would command about 25 cents per pound in the marketplace. An eventual market for desalination processes in excess of $150 million is predicted for the cheese industry; perhaps 10% of this might be expected to materialize before 1975, according to the study (*see chart*).

The potential market in **the pulp and paper industry** is greater than in any other, says the osw study. $75 million worth of electrodialysis equipment alone is predicted for use in recovering organic compounds from spent sulfite liquor (see also ES&T, November 1969, page 1147, for an account of the use of electrodialysis in the pulp and paper industry). Even larger markets are foreseen for reverse osmosis in the treatment of bleach plant effluent and dilute wash water.

The iron and steel industry could benefit from the use of electrodialysis techniques in the treatment of spent pickle liquor, according to the study. The total industry market is estimated at $140 million. (Alternative processes for the recovery and regeneration of pickling acid and iron are described in ES&T, May 1970, page 380.)

Electrodialysis also has a large potential market in **the plating and metal finishing industry,** where spent plating solutions and rinse waters must be treated to remove metals and toxic acids. (Electrolysis techniques, too, are being pushed into this market— ES&T, March 1970, page 201, describes one such process.) The market may be as big as $50 million, says osw.

Evaporation (not exclusively a desalination process, of course) is seen as representing a potential $50 million market in the **nuclear power generating industry** and a possible $400 million market in the treatment of **acid mine drainage.**

In all, Aqua-Chem's study predicts the existence of possible markets worth almost $1.5 billion for evaporation, reverse osmosis, and electrodialysis processes, with almost 10% of the market realizable within the next five years. Whether this exceedingly large market is as tangible as equipment makers might hope remains to be seen, of course. But Bovet emphasizes that the Aqua-Chem study ferreted out only those instances where revenue from by-product sales would equal or exceed operating expenses, including amortization of the initial capital investment. In other words, osw feels that these markets can be penetrated without any need for additional laws against water pollution. Should laws tighten further—as they probably will—the potential markets will be even greater. And, Bovet continues, the great possibilities in the giant chemical and petroleum industries were not even considered in the Aqua-Chem work.

What must be considered as a counterweight to boundless optimism regarding the osw projections is the absolute certainty that, if the markets do indeed develop, desalination processes will not have the field to themselves. As ES&T readers will be aware, a whole range of alternative techniques is already being lined up to take advantage of any move by industry to recover its by-products or otherwise defray the costs of water pollution control.

Desalting processes have market potential in several industries

Cheese Industry

market size $ millions

1970 1975 1980
year

Pulp and paper Industry

market size $ millions

1970 1975 1980
year

Source: Office of Saline Water

☐ electrodialysis ■ reverse osmosis ▨ evaporation
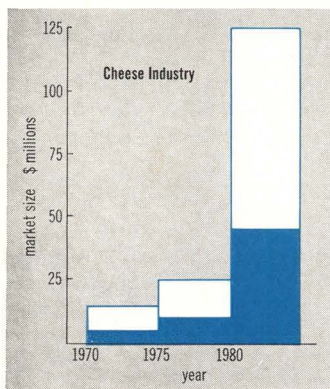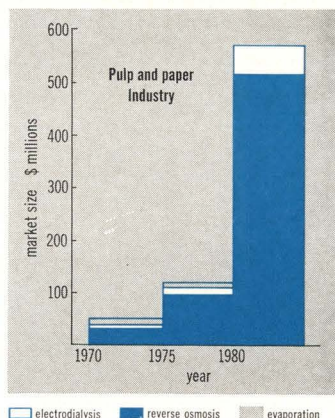
Air pollution: plant killer

*Polluted air is responsible for
vegetation damage costing the U.S.
a half billion dollars yearly*

In June a University of Delaware agricultural scientist noticed an excessive number of leaves dropping from potato plants in an open rural field. On closer inspection he noticed small, white spots on the upper surface of the leaves. This mysterious "blight" occurred following a period of extremely high ozone levels in the atmosphere.

One of the increasing environmental concerns today, shared by government, industry, and the private citizen, is the effect of air pollution on vegetation. The amount of pollutants released into the atmosphere is presently 142 million tons annually, and the U.S. Department of Agriculture (USDA) states that agricultural losses up to $500 million per year are being caused by increasing air pollution levels. California alone suffers a loss of $100 million annually. Causing detrimental changes in the agricultural economy, the rising pollutant concentrations threaten the truck farming economy around Los Angeles as well as the Connecticut cigar-wrapper tobacco industry. In New Jersey, air pollution damages over 57 different plant species and has become the worst single problem in the northern part of the state.

Acute and chronic damage

Plants, like people, are sensitive to air pollutants, and exposure to these harmful gases in the atmosphere results in vegetation injury. Not only do incidents of high air pollution cause visible damage, but also chronic, sublethal levels of air pollutants contribute to the weakening and eventual destruction of a plant's physiological life processes. Both the acute incident and sublethal levels adversely affect the growth, productivity, and quality of vegetation.

As with pathogenic diseases, the extent and nature of injury or damage are determined by genetic, climatic,
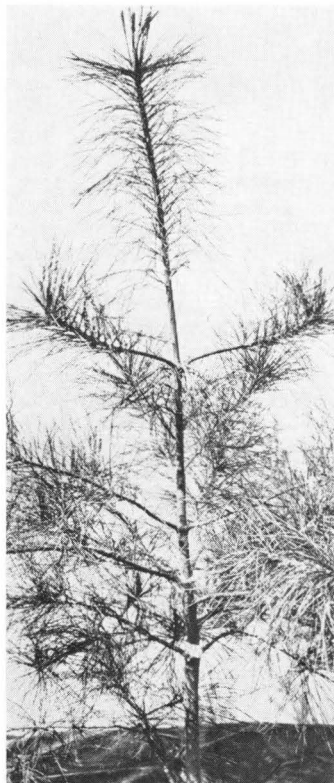
Stunted. *Ten year old pine will die*

and meteorologic factors as well as by level and duration of exposure to various types of pollutants. USDA plant pathologist Howard Heggestad states, "Most of the (monetary) loss is due to growth suppression or chronic injury; however, the acute injury suggests the nature of the air pollutant and reveals the distribution of the problem." Each pollutant or combination of pollutants is prone to produce its own pattern of injury, leaving graphic records of pollution episodes.

Al Wood, Penn State University pathologist, has devised a useful classification of pollutants that are pathogenic to plants. Wood divides pollutants into two types:

• Primary pollutants are those which are phytotoxic (lethal) to plants as they originate from the source.

• Secondary pollutants are those which do not originate at the source but are formed through reactions of pollutants from the source.

Reactions which form secondary pollutants can occur at the emission point or in localities removed from the source, depending upon the rate of reactivity of the compounds involved.

The major gaseous pollutants in the United States today, adversely affecting vegetation, are sulfur dioxide (SO_2), hydrogen fluoride (HF), ozone (O_3), and peroxyacetylnitrate (PAN). Sulfur dioxide and hydrogen fluoride are primary pollutants, while ozone and peroxyacetylnitrate are secondary pollutants.

Sulfur dioxide

What are the sources and symptoms of air pollution damage to vegetation? Unfortunately, there are no simple answers to the question. Sulfur dioxide originates principally from these sources: • the combustion of coal; • the production, refining, and utilization of natural gas and petroleum; • manufacturing and industrial utilization of sulfuric acid and sulfur; and • the smelting and refining of ores, particularly lead, copper, nickel, and zinc. The most important single source of sulfur dioxide is represented by coal-burning power plants, and numerous incidents of vegetation damage have been reported in these localities.

Sulfur dioxide injury to foliage may be acute or chronic; the toxicity of sulfur dioxide is a function of the rate at which it is absorbed. Acute injury occurs when the pollutant is absorbed at

a rapid rate, and chronic injury is caused by long-term absorption of sulfur dioxide at sublethal levels. When this effluent is absorbed by the leaf tissue, areas of the leaf die, dry out, and usually bleach to a light tan or ivory color. More severe dosages result in complete bleaching of the leaf. Vegetation may be affected by sulfur dioxide when ground levels exceed 0.3–0.5 p.p.m. In one area of Tennessee, sulfurous fumes from copper smelters left 17,000 acres of ground essentially void of plant life.

Major sources of plant-pathogenic air pollutants

Pollutant	Source				
	Transpor-tation	Industry	Generation of electricity	Space heating	Refuse disposal
	(million tons/year)				
Sulfur oxides (SO$_2$)	1	9	12	3	<1
Hydrocarbons (O$_3$, PAN)	12	4	<1	1	1
Nitrogen oxides (O$_3$, PAN)	6	2	3	1	<1
Fluorides (HF, SiF$_4$)		<1			
Others	<2	8	<4	<2	<2
Total	<21	<24	<20	<7	<5
%	28	30	26	9	7

Source: Restated from F. A. Wood, 1968. "Sources of Plant-Pathogenic Air Pollutants," *Phytopathology* **58** (8), 1075-1084.

Fluorides

Some fluorine-containing compounds, such as HF and silicon tetrafluoride (SiF$_4$), are emitted from the following processes: • aluminum reduction processes; • manufacture of phosphate fertilizer; • pottery and ferroenamel works; • brick plants; • refineries; • steel manufacturing plants; and • rocket fuel combustion. Although the actual tonnage produced is lower than other pollutants, fluorine is toxic at much lower concentrations (0.5 p.p.b.) and also acts as a cumulative poison. Fluorine is readily absorbed and translocated to leaf tips and margins and remains in a soluble form, retaining the chemical properties of free, inorganic fluoride. Aside from the injury to vegetation, there is potential danger to animals or even human beings feeding on plants high in fluoride content.

Injury from fluoride may appear in a few hours but more commonly appears after several weeks of exposure. On most broad-leafed plants fluoride causes tissue to die at the margin and tip of the leaf. The dead tissue may be gray or light green at first, later becoming reddish-brown or tan. As exposure continues, the entire leaf may die and fall off. Near Spokane, Wash., ponderosa pine was killed over a 50-square mile area by fluorides from an aluminum ore reduction plant.

Ozone

Ozone, a typical secondary pollutant, is derived from the upper atmosphere, electrical storms, and photochemical reactions. Although ozone can be carried from the troposphere or develop in thunderstorms, the most important source of this pollutant is a series of photochemical reactions in polluted atmospheres. Oxides of nitrogen and hydrocarbons that are emitted by automobiles, industries, and utilities react in the presence of sunlight with

oxygen to form ozone, as indicated in the following general reaction:

$$NO_2 \xrightarrow{\text{Light}} NO + O$$

$$O + O_2 \xrightarrow{\text{Light}} O_3$$
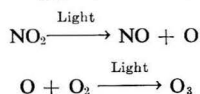
The amount and speed of ozone build-up depend upon the type of hydrocarbon, concentration of hydrocarbon, concentration of NO$_2$, irradiation time, and the amount of ozone produced.

Typical patterns of ozone injury are bleached or light flecks or stipples (small clusters of dead cells) on the upper surface of leaves. Fully expanded, mature leaves are most sensitive to and are most readily damaged by ozone. Emergence tip burn, a disease of white pine, had puzzled foresters and pathologists for years. Recently, the presence of ozone correlated with the occurrence of this disease. Concentrations below 0.05 p.p.m. will cause injury symptoms on sensitive plant species.

PAN

The other major secondary pollutant is PAN, which is a member of a homologous series of compounds that originate from the reactions of unsaturated hydrocarbons and oxides of nitrogen in the presence of light as in the following general equation:

$$Olefin + NO_x \xrightarrow{\text{Light}} CH_3COONO_2$$
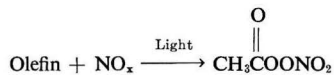
PAN or related compounds are formed in this manner, depending upon the type of olefin involved, the presence of NO$_2$, and the irradiation time. Natural sources of hydrocarbons, such as terpenes that evolve from coniferous vegetation, in the vicinity of man-made sources of hydrocarbons have the ability to react photochemically and produce PAN, thus complicating control efforts.

PAN injury is characterized as glazing and bronzing of the lower leaf surfaces and attack of the younger leaves. Eventually, the leaf tissue dies, leaving dead areas in the undersurface and sometimes through the leaves. Concentrations of 0.02–0.05 p.p.m. PAN for a few hours are sufficient to cause injury to vegetation.

Combined effects of two or more pollutants, such as ozone and sulfur dioxide in sublethal concentrations, may well result in more severe reactions than with either pollutant alone. Because details of synergisms are not yet fully explored or understood, continuing investigations are aimed in this direction.

Pollution-resistant plants

Since increasing costs and losses are being passed on to the consumer, the effects of air pollution damage to vegetation have yet to be fully ascertained or economically determined. Industrial researchers and agricultural scientists in government sponsored research programs are investigating the nature and prevention of or cure for pollution damage to vegetation. Extensive breeding programs have been initiated to develop and maintain species of crops that are genetically resistant to atmospheric pollutants.

Also, utilizing the idea of protecting vegetation from harmful effluents, researchers are working with antioxidants, growth regulators, transpiration suppressants, and other chemicals. Application of these compounds would allow growth in the presently polluted atmosphere until concentration reduction is significantly successful.

These programs are attempting to adjust to the present situation before nationwide pollution controls are adequately effective. However, until abatement procedures obtain results in reducing air pollution levels, the injury to vegetation will continue.

Chemicals, bugs tame process wastes

*Combination of coagulation and
activated sludge treatment cleans
up plastics plant effluent*

More than 90% removal of biochemical oxygen demand (BOD) is being achieved by a $1 million waste water treatment plant newly started up by the B. F. Goodrich Chemical Co. in Pedricktown (N. J.). The facilities in the polyvinyl chloride (PVC) plant are, according to Goodrich, the most advanced of their type in the PVC industry and were financed to the tune of $364,900 by the Federal Water Quality Administration (FWQA). Partial funding by FWQA was contingent on Goodrich sharing its treatment plant design and know-how with other companies in the PVC business during the first year of plant operation.

The Goodrich PVC plant in Pedricktown is the company's sixth and represents a multimillion dollar investment for the world's major vinyl raw material producer. Emulsion, suspension, and bulk polymerization processes used at the plant are based on vinyl monomer manufactured by Goodrich in Kentucky. Water is supplied to the plant from nearby wells and deionized before use if needed for process purposes. Process effluent comprises the bulk of the waste stream that requires treatment before discharge to a tributary of the Delaware River.

Design criteria

The waste is milky white and contains various (and varying) amounts of monomers, polymers, dispersants, organic and inorganic salts, etc., in both dissolved and suspended forms. Goodrich personnel studied raw waste from other PVC plants before construction of the Pedricktown plant, and the following parameters were found typical:

	(mg./l.)
5-Day biochemical oxygen demand (BOD_5)	720
Chemical oxygen demand (COD)	1285
Total solids (TS)	2000
Suspended solids (SS)	1000
Volatile suspended solids (VSS)	950

It was recognized, too, that these figures were highly variable due to process fluctuations.

The waste treatment plant was designed so that discharged effluent conformed to regulations stipulated by the New Jersey Department of Health and the Delaware River Basin Commission (DRBC). Chief among these requirements were:

• A minimum of secondary treatment must be provided, regardless of the quality objective for the affected stream.

• Discharges cannot contain "more than negligible" amounts of floating material, suspended matter which will settle to form sludge, toxic substances, or substances (or organisms) that produce color, taste, odor of the water, or taint fish or shellfish flesh.

• BOD reduction must be at least 85% (30-day average).

Goodrich therefore aimed at 90% reduction of ultimate BOD under winter conditions (13° C.) and based design criteria on a waste water flow of 800,000 gallons per day (g.p.d.) and the effluent characteristics listed above.

Two years were spent in research and process design for the final process now on stream at Pedricktown. Goodrich received technical assistance from Roy F. Weston and Associates (West Chester, Pa.).

It was decided early in the game that waste equalization facilities would be needed because variations in organic loading (the quality of the waste water) and in hydraulic loading (the actual volumetric flow rate) were expected. Research also showed that a preliminary step for latex solids removal would have to be included, since the presence of such solids materially reduces the efficiency of biological treatment. The waste was otherwise found to be nontoxic to a biological treatment system.

Alternatives rejected

Activated carbon adsorption was considered as a means of reducing BOD, but adsorption capacities proved poor, a factor attributed by Goodrich engineers to the presence of long-chain organic soap molecules in the waste. Contact stabilization and trickling filter systems, too, were considered but rejected. The method chosen was a completely mixed activated sludge system, which uses a biological floc similar to that conventionally used for domestic sewage treatment. (In fact, the seed material with which the Pedricktown treatment plant started up was obtained from a municipal plant at Haddonfield, N. J.)

Primary treatment

Although the PVC plant at Pedricktown is not yet on stream at full capacity, the waste water treatment plant is completely built and is at present treating an estimated 250,000 g.p.d.

Waste water from the polymerization process units enters first a 950,000 gal.-capacity stirred equalization tank, sufficient in size to provide one day's detention time at design throughput rate. The first treatment step (*see*
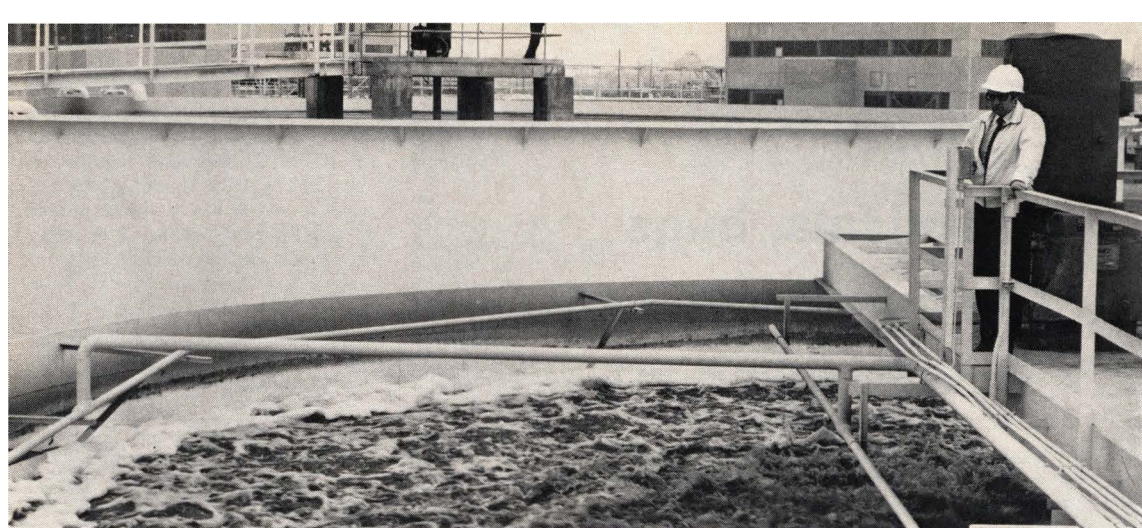
Biological. *Two 178,000-gal. aeration tanks treat* PVC *waste water at Goodrich* PVC *plant*

flow sheet) is the addition of coagulant and coagulant aid in a two-compartment flash mixing tank. The ferric chloride coagulant is added to the waste, at a dosage of about 150 p.p.m., before the coagulant aid—a polyelectrolyte, either Calgon 227 or Nalco 670—is mixed in at a dosage of 1 p.p.m. About two minutes detention time is provided for mixing in each compartment. The waste then flows to the primary clarifier in which the flocculated solids settle out. This "chemical sludge" is drawn off from the bottom of the primary clarifier and is thickened (from 2.5% to 8% solids) in a separate tank.

Secondary treatment

Clean supernatant from the clarifier is pumped to one of two 178,000-gal. capacity biological aeration tanks in which the oxygen-demanding components of the waste are consumed by bacteria contained in an activated sludge mass. To the supernatant are added small amounts of phosphoric acid and ammonium hydroxide which supply the sludge bacteria with nutrient phosphorus and nitrogen. (Domestic sewage normally contains enough of these essential elements to eliminate the need for nutrient addition.) Caustic soda is also added just prior to the aeration tank to keep the pH above 7.0—the $FeCl_3$ used as coagulant tends to acidify the waste, and at a pH below 7.0 filamentous organisms form at the aeration stage. Ten hours detention time is provided at this stage. Overflow from the aeration tank goes to a secondary clarifier (the plant has two) in which sludge solids—"biological sludge"—settle out.

Some of this sludge is recycled to the aeration tank and the excess is thickened in a separate tank. Overflow from the secondary clarifier runs into a polishing lagoon which also receives storm runoff from the plant. Although some additional BOD and suspended solids removal may be expected in the lagoon, the secondary clarifier effluent is fully treated, and the lagoon discharges directly into the nearby tributary of the Delaware.

Solids disposal

Settled sludge from both chemical sludge and biological sludge thickeners is centrifuged and dewatered to about 45–50% solids. The dewatered sludge is inert and is trucked to a landfill, while the filtrate is returned to the equalization tank.

The plant is working well. Representatives of several other PVC-producing firms have studied the Goodrich treatment system and FWQA officials hope some of these firms may be able to adopt similar systems. Goodrich aims eventually at 100% reuse of its water supply but further treatment of the lagoon effluent will be necessary to meet its stringent requirements for process water. Even so, the present secondary treatment system has proved capable of removing 93–98% of the BOD from the PVC plant waste water.

$500 million market for air monitors

*Industry spending, emission source measurement predominate in
ten-year forecast of markets and R&D needs*

Industry is expected to be the major purchaser of air pollution control instrumentation over the next decade and will account for 70% of the total expenditures, according to a survey of this market being conducted for the National Air Pollution Control Administration (NAPCA) by Esso Research and Engineering Co. Of the estimated $469 million that will be spent for such instruments, industry will account for about $346 million, says Rene Bertrand, an Esso chemist involved in the study.

These conclusions were presented in an interim report on the Esso–NAPCA survey at the annual meeting of the Air Pollution Control Association (APCA) in St. Louis. The study itself and the final report are not scheduled to be completed until October, when a companion Esso–NAPCA report on research and development needs will also be published.

The Esso analysis breaks down the air pollution instrumentation market into three major forecast areas: Ambient level measurement, stationary source emissions, and auto exhaust monitoring. Bertrand told the APCA meeting that "the market is predominately one of stationary source emission measurement," which alone accounts for almost 50% of the dollar total. The remainder is fairly well distributed between ambient level and exhaust monitoring. Bertrand admitted that the stationary source segment of the market was extremely difficult to predict because of a lack of historical data. Even so, the estimate is probably conservative in that it assumes a minimum of measurement by industry. Furthermore, the forecast was drawn up within the framework of current air quality legislation, which places main emphasis on the ambient air quality level. Accordingly, it does not take into account the potential increase in the market that could result from adoption of national emissions standards.

1970-1980 air pollution instrumentation market

Auto emissions monitoring
$143 million 29%

Ambient level monitoring
$78 million 22%

Stationary source monitoring
$248 million 49%
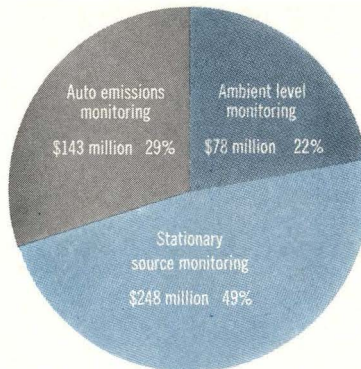
Total market $469 million

Development of the $248 million market for emission source monitoring is expected to have a slow but steady growth, based on the postulate that measurements will not be required unless there exists a feasible control technique to which the measurements can be directed. Thus, the growth curve for this market will hit its peak rate later in the decade, after wider use of control technology.

Specific pollutants

Particulate monitors lead the list of new installations for specific pollutants; projected demand is 7125 units at a total cost of $60.5 million. Somewhat surprisingly, the study lists NO_x monitors as the second largest category, with a forecast demand for 6600 new units at a total cost of $26.4 million. Other new markets include SO_2 monitors (3150 units, $12.6 million) and hydrocarbons (3600 units, $1.5 million). Industry expenditures will account for $226 million of the total ten-year expenditures of $248 million for source monitors.

Just as industry purchases will dominate the market for source emission monitors, the market for ambient level measuring instruments will be paced largely by control agencies. In one respect, the ambient monitoring market was the easiest to delineate, largely because, as Bertrand points out, there exist at least some historical data on which to extrapolate future trends. Primary sources for the study were the existing and future plans for state and local control agencies in the Middle Atlantic states and California.

Little correlation was uncovered in these areas between the number of continuous air monitoring stations and such factors as geographical area, local population density, and industrial concentration. On a regional scale, however, one rule of thumb appears to be a requirement for 3.7 continuous air monitoring stations per million population. This leads to a forecast for an additional 600–700 state and local stations and 100 federal installations.

Largest sector

Continuous air monitors are expected to be the largest sector in this field, and will account for $35 million. But relatively simpler instrumentation will fill a significant part of total agency requirements for ambient monitoring, accounting for $33 million by 1980. Industry will be a small but significant customer for ambient monitoring systems, for two reasons: Some control agencies will probably require industries to monitor ambient levels surrounding their facilities; at the same time, industry will undoubtedly conduct some voluntary monitoring both to demonstrate a concern for clean air and to provide documentation against indiscriminate complaints. Industry purchases in this area over the coming decade are pegged in the report at $10 million.

The market for ambient level measurements is expected to build rather steadily and reach its peak in 1972.

Time frame for air monitor market
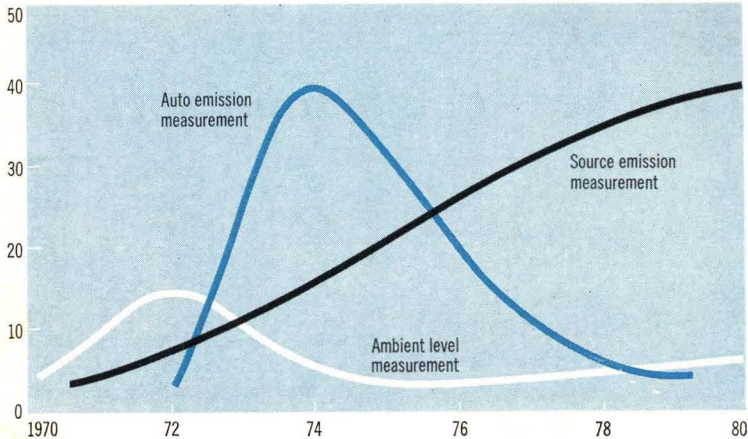
Source: Esso Research & Engineering

Bertrand based this estimate on an early designation of control regions by the federal government, which should enable establishment of most control agencies within the coming year. "Following an initial period of instrument purchases to set up monitoring networks, which we estimate will be completed in 1972, we anticipate that the yearly market for this area of instrumentation will be considerably reduced in the remainder of the decade," said Bertrand. Past trends indicate agency expenditures for instrumentation usually level off at 3% of their total budget, and the annual replacement market will be about $3 million from 1974–80. Industry expenditures will also peak early in the decade; later, industry is expected to concentrate on stationary emissions monitoring.

Auto monitors

Bertrand pointed out that the auto emissions monitoring market is perhaps the most controversial at the present time. He therefore considered it more significant to develop a high estimate as the most useful parameter, one predicted on the adoption of an annual nationwide exhaust control inspection program. The market thus generated would consist of an agency segment of $33 million, required for individual states to gear up motor vehicle inspection lanes to check emission control devices annually, and an industry segment of $110 million, represented by service station facilities to make necessary adjustments to engines and control devices.

Bertrand stressed that this industry segment will only come about if instrument manufacturers develop a low cost inspection system, perhaps in the vicinity of $500 for a simple package. By and large, the auto emissions monitoring market will develop rapidly, when it comes. Esso Research presents it as peaking in 1974, although the peak could occur anywhere in the 1974–76 period. One of the reasons for the projected rapid growth is the increasing probability that federal statutes regulating auto exhaust emissions will make grants available to the states to implement an inspection and testing program. Such legislation, S. 3229, is now pending before Congress; if this or a similar proposal becomes law, there will be a short period when states will establish testing facilities, the market will build rapidly, and then disappear almost as fast.

R&D needs

As to the state-of-the-art, also being studied at Esso Research and Engineering, there appears to be a need for advances across the whole spectrum of monitoring areas. H. J. Hall, one of the investigators responsible for this phase of the study presented a companion paper, coauthored by N. L. Morrow and NAPCA's R. S. Kirk, at the APCA meeting. He said that "there are a number of instances where satisfactory instrumentation is not available for standards which have already been set or are expected in the near future," such as auto exhaust particulates, NO_x emissions, and low levels of ambient oxidants. Furthermore, data are needed for new or modified criteria, while instruments needed to make the necessary measurements are not fully developed. Examples here include aeroallergens that can now be measured only by microscopic counting and respirable particulates.

Hall explained that up to now ambient level measurements have been considered most important in the U.S. to serve as the basis for standards, and to find out where we are now, compared to where we were some years ago. The major problem in designing instrument R&D programs has been considered how to make these measurements at progressively lower levels.

Devices for cumulative measurements of ambient levels, excepting sulfation plates and particulate samplers, are unsatisfactory, says Hall, and there are possibilities not yet fully exploited, such as the development of solid absorbents instead of liquid bubblers for field samples. For the long term, one way to simplify instrument requirements would be development of long path analyzers for measuring average concentrations across an entire city or industrial area. This type of approach would substantially reduce the number of instruments required, and suitable instruments could be immediately applied with present standards.

The need for real time measurements for pollution alert warnings is limited to a few pollutants and can be met by instruments without the sensitivity required for low ambient levels, Hall found. He maintained that it is simpler to consider the dynamic system as a whole, either by chromatographic techniques, selective adsorbents, or spectrometers.

Regarding monitoring stationary emission courses, the most persistent problem is sampling stack gases at stack conditions, particularly for compliance testing. Present methods of stationary source sampling are cumbersome and time-consuming, and data required to set new standards are often poorly defined. Looking to the future, remote stack monitoring techniques such as laser back-scattering are expected to be of great value.

Final decisions on developing specific hardware for monitoring auto exhaust emissions probably depend on a more exact definition of needs, according to Hall, because of different approaches being taken by various states. N.J., Del., and D.C. are planning for annual inspection of control devices, while other states, such as California, are apparently considering a program of going for spot compliance testing by highway patrolmen.

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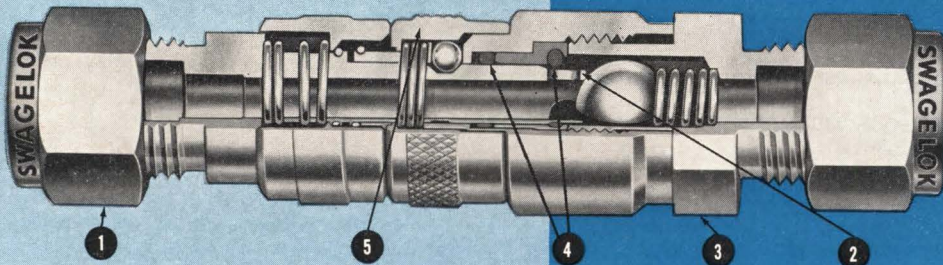
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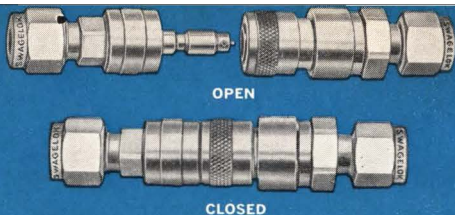
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Underground waste disposal:

Waste injection wells are becoming popular but the field
is still plagued by some fundamental misunderstandings

Deep-well disposal has become a controversial topic, at least to the environmental control engineer, his associates, and much of the general public. However, in view of the wide potential for useful application of subsurface fluid, gas, and solid handling techniques to water and air resource conservation problems, the subject should be of interest to every practicing engineer, as well as to those engaged in other phases of environmental control work. Deep-well disposal of liquid wastes is really only one small part of a wider field—the application of subsurface geologic technology to natural resource conservation.

While there will be some simple arithmetic presented here, I will not attempt the usual translation of logic into extensive engineering mathematics for computerized application. Unquestionably, computer technology is a tremendous asset to the engineer and enables us to construct, almost instantaneously, a massive, inverted, pyramid of rapidly expanding confusion balanced neatly upon any initial point of irrelevancy that can be expressed by a numerical symbol. But it will be my purpose here only to point out some of the broader, overall aspects of the subject of subsurface considerations. A few points of technical relevancy will be illustrated, and thereafter those who so desire will be free to construct their own pyramids.

Practically speaking, deep-well disposal is, at the moment, the one facet of subsurface technology that most engineers are probably familiar with, and my discussion will start with some comments on this specific method, particularly regarding areas in which a review of current literature indicates some fundamental misconceptions.

Origins

The process actually originated in the petroleum industry over 40 years ago as a means of disposing of salt water that commonly accompanies oil taken from producing wells. The original reason for this was probably the well-known fact, at least in the oil field, that salt water has an amazing affinity for any expensive cows! Later, the concept of using this water to increase oil recoveries developed and then the process of "secondary recovery," or "water-flooding," was born. Geologists then developed a broad spectrum of engineering data regarding the injection of fluids into subsurface geologic formations of various lithologic character. Concurrently the concepts of repressuring exhausted oil fields with gas came along, and once again a backlog of engineering data on injecting gases into geologic formations began to develop. This has been further accelerated by the development of underground gas storage facilities. Both these techniques may well have application in alleviating air pollution problems in the future, and research should be initiated on this possibility.

Within the last 15 years, with the growing problems of industrial waste, the use of these subsurface techniques for industrial and municipal waste disposal began to develop. The first industry outside the petroleum companies to use this technique was the chemical process industry, probably because operation of specialized oil field service divisions allowed chemical process engineers to become acquainted with these concepts. By about 1965, the boom was on. Because of a rapid proliferation of waste disposal problems, particularly with toxic or difficult-to-treat wastes, underground disposal was attempted by industries of all types. Some of these attempts were successful, others were not.

No accurate figures are available, due to variations between different states and companies in reporting requirements, but it appears there are about 40,000 saltwater injection wells operated by the petroleum industry in the U.S. either for brine disposal or secondary recovery purposes. There may be another 1100 fluid injection wells involving waste disposal, groundwater recharge, and protection against saltwater invasion operated by various industries and municipalities. In addition, the petroleum industry uses about 20,000 gas injection wells for reservoir maintenance purposes, secondary recovery, or underground gas storage.

If we consider the additional tens of thousands of wells that have been involved in extracting oil, water, gas, sulfur, and salt from beneath the earth's surface, it's apparent that the massive backlog of data regarding subsurface geologic techniques can be of primary interest and a useful tool to all involved in the problems of natural resource protection under many combinations of circumstances.

Pros and cons

As is true of any engineering system, there are advantages and disadvantages involved in the use of these methods. It is the engineer's job to weigh the factors involved in coming up with a workable solution. Advantages of subsurface techniques to water resource problems under good geologic circumstances are:

- A potential method of ultimate disposal, in the sense that wastes untreatable by other means may

concepts and misconceptions

be permanently removed from our immediate environment, in most cases, and for very long times in others. With proper system design, the length of anticipated storage time can be relied upon to provide neutralization of the waste by the continuous normal geochemical and geohydrological processes long before the waste would ever migrate to the surface.

- Protection of fresh groundwater supplies from saltwater invasion.
- Underground storage of fresh water in arid regions to reduce evaporation losses, or to store intermittent freshwater supplies.
- Groundwater recharge in areas heavily dependent upon groundwater sources as a water supply.
- Solids storage and disposal under some conditions.
- Effective use in conjunction with other water supply or waste disposal processes. This may be particularly true when a waste of small volume is highly dangerous or toxic, and the cost of treating the waste by usual means may make effective treatment of the total flow impossible. In such cases, it is frequently feasible to separate the high pollutant level waste stream from the main waste flow and dispose of it underground at less cost than trying to pay for treating the entire flow on the basis of the combined pollutant levels. Where the water supply problem is more critical than waste disposal, it is frequently feasible to apply additional treatment to effluent from a secondary waste treatment plant and inject it back for later use.
- Potential solution to some air pol-
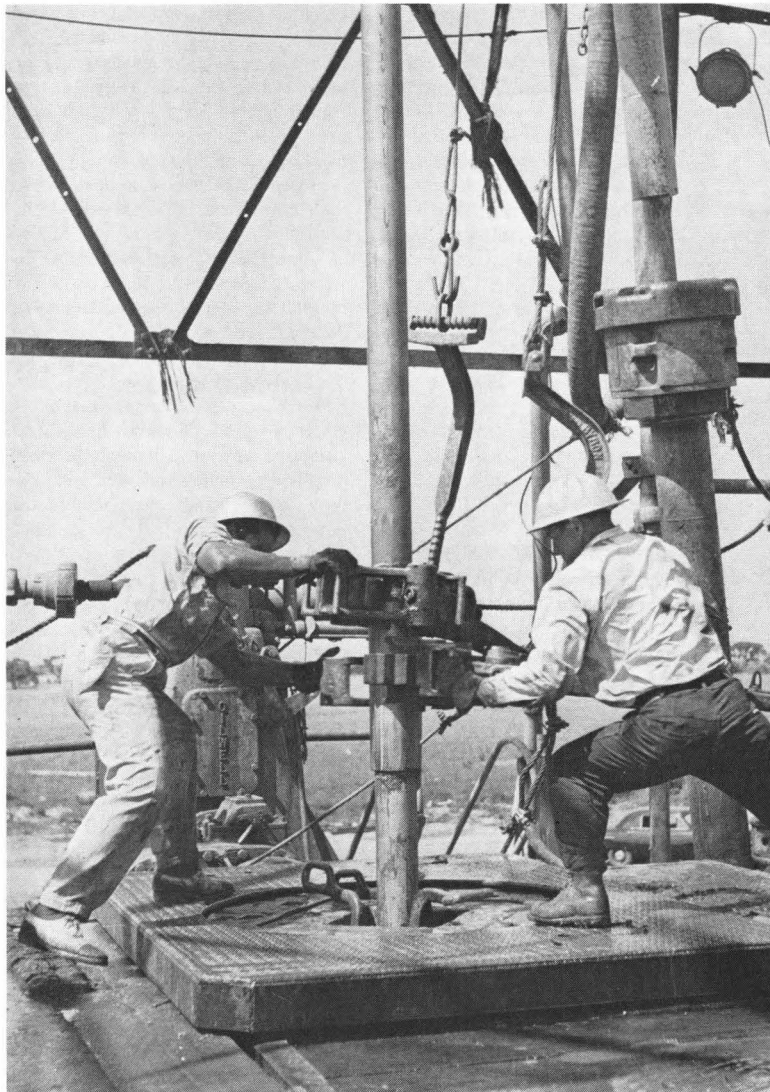
Drilling. *Oilfield technology often can be used for natural resource protection*

lution problems, as injection of toxic or otherwise obnoxious fumes into underground storage reservoirs.

The foregoing advantages are sometimes offset by several disadvantages, the most important of which might be:

- Existence of unfavorable geologic circumstances in the vicinity of the problem. This factor alone places some rather severe limitations in many areas.
- Fluid incompatability, in case of liquid injections, between the natural formation fluid and the fluid being injected.
- Possible loss of control of the waste liquids after injection.
- Legal problems that may arise from such activity. For example: when does underground trespass start? What are the degree and extent of the injector's liability in the event of surface or subsurface damage to nearby properties? Who owns water injected in groundwater recharge? There are, of course, many other problems of this type that will arise as usage of these methods increases. Obviously, the use of subsurface techniques for industrial wastes has not been widespread enough to have built up much in the way of legal precedent; many of the petroleum and water rights laws on the books are rarely precisely applicable to the industrial waste disposal problem.

Finally, there is a tremendous problem involved in educating regulatory bodies, the body politic, and the industrial users to understanding the design and operational principles and limitations inherent in the application of these subsurface techniques to the field of water and air resources. Sometimes it seems that the necessity for the application of a certain amount of thought and intelligence to utilization of underground techniques is probably their greatest disadvantage.

Well design

The field of underground fluid or gas handling has two major divisions—the surface factors and the subsurface factors. To put it simply, the first basic requirement for underground disposal is a usable hole in the ground. This involves a geologic study for determination of a specific location and the operation of drilling equipment. In most cases, these factors

can be handled much more effectively by independent contractors intimately familiar with them, than by the usual design and construction engineer who normally specializes in surface structure construction. The drilling, testing, and casing program of a well, if properly done, will establish the volumes of fluid it can effectively accept and the pressures required to maintain these acceptable volumes at the desired rates of injection. Supervision of these phases of the project should be handled by a consulting geologist familiar with subsurface conditions. Once these data are acquired, the design of the treating and pumping equipment to prepare and handle the fluid at the surface, prior to injection, and the additional surface pumping equipment necessary to inject the fluid into the formation, can be handled by any capable engineer familiar with the basic principles of handling waste fluids or gases.

However, in the consideration of the subsurface factors, the average industrial project engineer is, usually, at somewhat of a disadvantage by virtue of background training and normal experience. For this reason, illustration of a few basic principles involved in the subsurface functions of the fluid handling system might be of both interest and value to the engineer involved in the overall supervision of any environmental control problem involving underground disposal, even though this phase of the project should normally be handled by a consultant.

The areas in which current literature indicates some misunderstandings are injection pressure requirements, hydraulic fracturing techniques, formation fluid capacities, and fluid migration conditions. An attempt will be made to use, as illustrations, examples involved in these areas. So we must go "down the hole," so to speak, and take a worm's eye view of this system in order to discuss some of the mechanics involved at the bottom end of our "usable hole in the ground."

Migration rates

First, let's consider briefly the question of fluid well capacities and fluid migration in the geological formations. By assuming some typical parameters for a disposal well (*see inserts*), it can be calculated that a square mile of formation around the well could contain as much as 5,217,200,000 gallons

of fluid. If a waste fluid were injected at a rate of 10,000 gallons per day, it would take 521,720 days, or about 1429 years to fill up this space—and still move only one-half mile from the well site. By assuming a 50% saturation of the well by the original formation fluid, these figures would, of course, be cut in half.

Since a finely engineered disposal well would not use a receptor formation that outcrops nearby, it's apparent that under normal conditions of fluid migration it would take a long, long time for this material to reach the surface. Let us take, for example, an improbable situation in which our hypothetical formation might outcrop, or come to the surface, ten miles away from the disposal well. Using the 50% formation saturation figure, so that we only need 714.5 years to move the first half mile, we then find we still need 14,290 years for the injection fluid to arrive at the surface of the outcrop. Going one step further, just to be conservative, we might say that these figures are in error by 90% due to unknown factors affecting the migration rate, and that the actual migration occurs in 10% of our computed time. We still have a little over 71 years to move the first half mile and 1429 years to reach the outcrop.

If we add a dilution factor to account for mixing waste with the formation fluid, we are forced to conclude that it will take an extremely long-lived waste to reach an outcrop only ten miles away in its original form. In view of these factors above, it would seem wise to give more consideration to the use of underground formation space for storage, treatment, and ultimate reduction of some types of pollutants.

Obviously, this total available space may not be available for storage at any particular location having these assumed porosity conditions. The determining factors here will be the percentage of saturation of the formation by naturally occurring fluid, and whether the acceptance of the injected fluid is achieved by displacement, diffusion, or a combination of both. The original formation fluid hydraulic conditions, hydrostatic or hydrodynamic, will also affect this factor of ultimate usable storage volume. It might be added here that observation of many core analyses and electric log data taken from drilling wells,
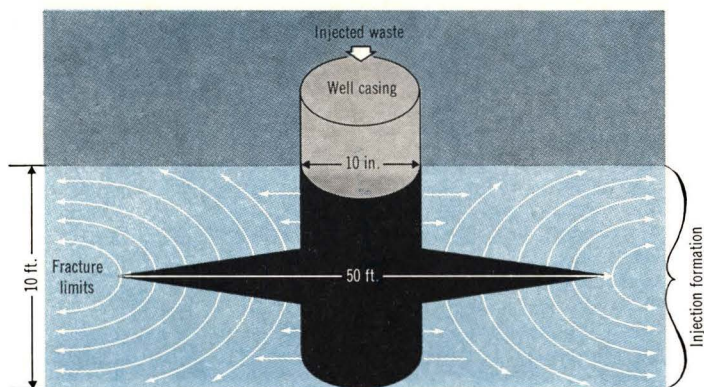
This simplified sketch illustrates several salient points about injection wells.

Well capacity: A formation of the dimensions indicated and with typical porosity (25%) and permeability (10 millidarcies) has a tremendous storage capacity, up to 8.2×10^6 gallons per acre of formation. As mentioned in the text, such a formation, in the absence of large amounts of naturally occurring fluids, can receive significant amounts of waste for literally hundreds of years without the fluid advancing more than a few miles from the well site.

Injection pressure: Injection pressure is a function of the effective pore space exposed to the advancing front of the injection fluid. As the fluid moves radially outward from the well, the surface area exposed to the fluid front (effective porosity) per unit volume of injected fluid increases. As a result, there is a rapid decrease in the injection pressure per given injected fluid volume and rate.

Fracturing techniques: If the formation surrounding the original bore hole is fractured, the net effect is to increase the initial surface area available for injection. For the 50-foot fracture indicated, each face of the fracture becomes a disk having 282,000 sq. in. of surface area. When this is compared with the initial surface area of 3768 sq. in. for the original 10-in. bore hole, it is easy to see why injection wells frequently "go on a vacuum" when fractured. The arrows show the fluid dispersion patterns around the fracture, from which it can be seen that channeling induced by fracturing will normally occur far beyond the limits of the original fracture.

ranging in depth from 1000 to 24,000 ft., has rarely shown formation fluid saturations in the 100% range.

The original formation bottom hole pressure will also have an effect on both injection pressure and the ultimate usable storage volume by virtue of the effect on the injection pressures required. Observation of many hundred drill stem tests at varying depths and across most of the Mid-Continent region has rarely indicated bottom hole pressures that even approached theoretical calculated hydrostatic heads for the depths involved. However, frequently in the unconsolidated sediments along the Gulf Coast, we do find theoretical hydrostatic and theoretical overburden pressures close to recorded pressures.

Fluid flow

Permeability, in practical terms, refers to the ability of the fluid to move through existing porosity, and thus into, or out of, the bore hole and on through the formation. This, in turn, tends to become a direct function of pore geometry by virtue of the normal friction resistance to fluid flow. Damage to the formation face in the bore hole by action of the drilling bit may also cause considerable modification of pore geometry as it affects fluid flow. As a matter of fact, in most cases most of the pressure required to inject fluid into a porous and permeable formation is really being used to overcome this combination of factors, causing high friction resistance only near the bore hole. This total friction resistance to flow is referred to as the "skin effect."

One of the great advantages of fracturing techniques lies in their use to alleviate this skin effect. Most of you are, no doubt, familiar with the appearance of the drawdown curve on

a water well, which looks something like this:
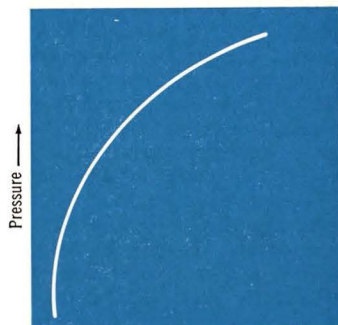
In other words, pressure required for a given fluid volume to flow at a given rate increases with decreasing distance from the well. The pressure curve for an injection well appears reversed but actually expresses the operation of the same physical factors:
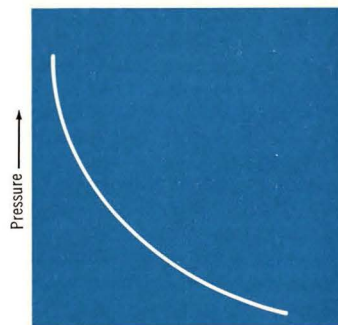
Here the greatest pressure required for flow is nearest the bore hole with a rapid decrease in required pressure away from the bore. To demonstrate the skin effect let us consider the fluid as moving through a series of ever-enlarging concentric cylinders as distance from the bore hole increases. If we assume an initial bore hole cylinder of 10 in. in diameter and a formation depth of 10 ft., the surface area of the bore hole cylinder is 3768 sq. in.

By the time the fluid has moved to a diameter of 20 in. from the axis of the bore hole, the total surface has become 7536 sq. in.; at 30 in. from the axis we have acquired an area of 11,304 sq. in. It can easily be seen that the steady increase in the cross-sectional area available to carry the fluid results in a very rapid decrease

of pressure required to move a given volume of fluid, at any given rate, into the formation. This condition will continue until the limits of the formation's geographic dimensions are reached or as long as the fluid is moving. Also, note that the pressure, volume, and velocity effects on the fluid flow are going to be constantly changing with the changing radius of flow around the bore hole. This point is very significant in terms of the potential of a disposal well to trigger earthquakes. Due to this rapid pressure drop it would take a very special set of circumstances for a disposal well to trigger a quake.

There are other factors involved in the flow mechanics that are pertinent to the skin effect, since they affect permeability, or "transmissibility:"

- Pore geometry as it relates to turbulence near the bore hole, and surface tension and viscosity of the fluid.
- Botton hole pressure of the original formation, which in some cases, exerts a back pressure on the injected fluid.
- Hydrologic conditions, whether static or dynamic.
- Percentage saturation of the original porosity by the in-place fluid, if any.
- Damage to the formation face by the original drill bit or infiltration of drilling fluid.

An interesting example of the combined effects on these factors occurred at the recent completion of a 3500-ft. well. In this case, an attempt was being made to hydraulically fracture a potential producing formation after a pipe had been set on top of the formation. The hole had been cleaned out, washed with mud acid, and the fracturing procedure instituted. Pressure against the formation increased to 8000 p.s.i. before the geologist gave the word to shut down because of the possibility of equipment damage. Not one drop of fluid had moved into the formation. The electric log and microlog indicated suitable porosity and permeability, and a drill stem test recovered only a few feet of oil-cut drilling mud, with no salt water. Thus, because a good shut-in-bottom hole pressure built up from 0 to 200 p.s.i., it was felt that the possibility of a blocked formation face existed.

For these reasons, it was decided to attempt an open hole perforation with large caliber expendable jet charges. The fracturing equipment was removed from the well, and when the perforating job was completed, another attempt made to fracture the formation was successful. The formation began to take fluid slowly at 900 p.s.i., fractured at 1650 p.s.i., and then took 2000 g.p.m. of sand slurry at an injection pressure of 300 p.s.i. The well was completed as a good pumping oil well for about 10 b.b.l. per hour with an operating bottom hole pressure of 420 p.s.i.g. Obviously the initial failure to pump into, or "fracture," the formation effectively was one due entirely to skin effect factors.

Misleading tests

The foregoing case is merely cited as an example of how great the effect of these factors can be when they are present in just the right combination. Pump tests on an injection well can also be misleading if initial pressure is simply accepted at face value, as evidence of the ability of a formation to accept fluids or the operating injection pressures required. In general, fracturing can cause a tremendous increase in fluid acceptability of a formation.

Unfortunately, hydraulic fracturing and its effects seem to be misunderstood factors in the underground disposal field. When interest in underground disposal began to spread, the first thing engineers apparently did was to research the petroleum field with respect to water injection wells. But there is a great deal of difference between a water injection well and a disposal well. The requirements are entirely different. The water injection well is used only in water-flooding for the purpose of secondary recovery. Under these conditions, the advance of the flood face must be kept as uniform as possible to provide a clean sweep of the in-place oil. This usually requires relatively low initial injection pressures, slow injection rates, and the absence of fracturing to avoid channeling and consequent bypassing of the oil in place in the vicinity of the well bore.

A saltwater disposal well is very different. Here it makes no difference whether or not the flood front is kept uniform; the problem here is simply to put as much fluid as possible into the formation at as low a cost as possible. This condition is much more similar to waste disposal than is water flooding. Under these conditions hy-
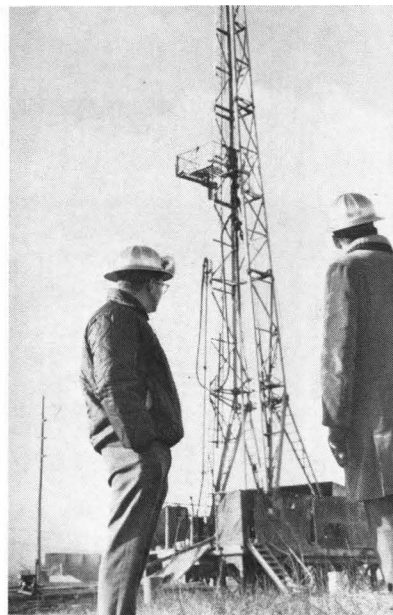
Derrick. *Drilling tests are critical steps in planning for waste disposal wells*

draulic fracturing is commonly used to increase formation fluid acceptability and reduce required injection pressures. Saltwater disposal wells are almost routinely fractured, and in the first year or two operate on a vacuum or gravity flow, and injection pressure buildup thereafter is at a very slow rate. In a waste disposal well a uniformly advancing floodfront is not needed, and the greatly increased expense required to maintain it can hardly be justified. (It should be added that hydraulically induced fractures do not close if the pressure drops. They are kept open by propping agents, such as sand or small beads, injected in a slurry as a part of the fracturing process.) Another very important misconception shows up in the often repeated comment that water produced with oil is usually injected back into the producing formation, thus more space is available. Quite the contrary is true, which points up how the difference in terminology between petroleum technologists and those not so familiar with the field can create misunderstanding. Where significant amounts of water are produced with oil, the oil is coming from a water-driven reservoir, already under natural flood, and injecting additional water into these sands would only cause possible channeling and consequent loss of oil. Thus, rather than waste money to gild the lily, water produced with oil from these reservoirs

is normally disposed of by injection into wells other than the producing horizon.

Water injection

The only place where water is normally injected into the same formation from which oil is produced is in the case of "water-floods" and these are only used to recover oil from reservoirs that contain no natural water drive. As a matter of fact, they normally contain very little or no waste at all. The water produced is that which has been previously injected. In this case water for flooding has to be obtained by drilling water supply wells to horizons other than the producing formation.

A misunderstanding of this key point seems to have led to many erroneous computations in the literature regarding available storage space and required injection pressures. It might well be said, as mentioned earlier, that failure to differentiate among some of these basic conditions appears to have led to the creation of some interesting pyramids of confusion, based on initial points of irrelevancy, with respect to the use of fracturing, available storage space, and calculated injection pressure requirements. There are various techniques of perforating, "shooting," acidizing, and hydraulic fracturing that can be used both to overcome the skin effect and to improve and maintain injective capability. It is, however, important to realize that the pressure required initially to inject fluid into an untreated formation is not necessarily a good index, of itself, of the pressure ultimately required for fluid disposal into that formation.

Of course, getting the fluid into the formation is only part of the problem—then comes the question of who is responsible for it. Although a considerable body of law has been built up regarding underground fluids and their migration, most of it has developed from our frontier day concepts of riparian rights and private property that have since been held to be applicable to petroleum and subsurface waters. Since underground waste disposal is a very new concept in legal terms, there has been little as yet in the way of precedents established for degrees of responsibility concerning migrated industrial waste.

There are, however, several mechanical factors known to be involved in any consideration of fluid migration in subsurface formations:

- Degree of formation cementation and formation porosity.
- Lateral extent of effective permeability and porosity.
- Characteristics of beds overlying and underlying the injection formation.
- The presence of faults and (or) fracture patterns in the area.
- Earthquake occurrence, frequency, and intensity in the area.
- Freshwater–saltwater contact levels are important in groundwater recharge, underground water storage, prevention of saltwater invasion, and finally, in regard to decisions specifying depth for projected waste disposal wells.
- Structural attitude of the injection formation.
- Hydrological characteristics of the disposal formation.
- Effectiveness of casing and casing cementing program.

It might be well to point out that this last factor is a point in injection well planning where great care must be exercised. While also true for producing wells, it is far more critical in injection wells due to pressure gradients resulting from the reversal of the direction of flow which the normal well casing program is designed to handle. The case of a disposal well "blow-out" at Lake Erie is well-known.

A review of published literature indicates that many disposal wells allow only for an inch of diameter differential between hole size and casing size. For example, 7.5- or 8-inch casing will frequently be set in a 9-inch hole. This allows a thin half inch film of cement between the casing and the formation. Since the cement-to-casing bond and the cement-to-formation bond usually represent the weakest link in the pressure retention chain, it would be well to specify, as a minimum, at least 2 inches of diameter differential between the casing collar o.d. and the hole for waste injection wells.

More knowledge

With regard to the present state-of-the-art of application of subsurface techniques to water resource problems and planning, there is an urgency for additional research in the foregoing areas to assist in establishing logical legal and operational principles by people familiar with both petroleum technology and industrial waste disposal techniques. For example, the field of suspended solids injection, an entirely new utilization of subsurface techniques, is an area in which there is still much to be learned. Some techniques have been evolved for the disposal of radioactive wastes, but even here much improvement is needed.

In addition, some successful experimentation is being done on the injection of sewage sludge solids into certain favorably constituted formations. The types of porosity and permeability required for high solids content fluid injection need to be further defined and determined. For example, the "lost circulation" zones, which oil well drillers unhappily experience, might well be feasible for waste sludge or slurry injection programs.

We might sum up by saying that subsurface injection has been used, either experimentally or on a large scale with varying degrees of success for a wide range of applications, shows that subsurface geologic techniques are important tools for the environmental engineer in his continuing struggle to meet the needs of society. It will pay him well to recognize the circumstances under which he may increase the effectiveness of his natural resource control and protection programs. After all, man is a very unique animal, the only one that is capable of destroying his own environment—and with it, himself. Whether he does this, or not, will ultimately depend upon engineers, scientists, and political leaders who must create, design, and build society's structures to protect the environment.

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A new approach to controlling biological processes

For years, because nothing better was available, the test for biochemical oxygen demand (BOD) has been the major parameter for determining the strength and controlling the treatment of waste waters. There are many problems with the BOD test, but its main limitation is the five days of analytical time required to complete it. This time requirement severely limits the usefulness of BOD as a parameter for development of design criteria for, and operation of, waste water treatment systems.

In addition, considerable confusion exists in the water pollution control field because BOD, as it is used, describes both the *food* and *energy* requirements, and even the culture content of biological systems. The distinction between "nitrogenous BOD" and "carbonaceous BOD" is but one example of this confusion between energy and food requirements which has developed from use of the BOD test. Separate parameters to describe these three distinct variables—food, energy, and culture—would lead to a simpler and more widely understood concept of the biological systems involved in pollution control work. This understanding would, in turn, lead to improved design and operation of treatment plants and better control of them.

Carbon cycle

Consider the fact that carbon is the basic building block of all living systems. It forms the molecular backbone of organic matter and is present in both organic and inorganic forms in all three phases of our hydrosphere—gas, liquid, and solid.

Carbon is also the basic food supply of living matter and is constantly changed from phase to phase by the biochemical and chemical reactions and physical processes of our biological systems. Without carbon, the universe would be sterile and void of any life form as we know it. Thus, not only is living matter composed mainly of carbon (about 85% dry weight), but carbon is also the major food item required for growth and maintenance of life. It is logical, therefore, that carbon should be a *primary* parameter for describing both the *food* supply and the *culture* content of microbiological systems.

Energy, on the other hand, is required in biological systems for conversion of carbon source to cell protoplasm and for maintenance of life in the absence of extracellular carbon. This energy is obtained through any of a variety of chemical oxidation–reduction reactions or through use of radiant (light) energy, as in photosynthesis. This energy requirement can be determined as the total change in oxygen demand of the system coincident with the conversion of carbon. Oxygen is also a significant factor in the quality of surface waters and is universally used to provide the energy requirements for biological treatment processes. It seems logical, therefore, to continue to use an oxygen parameter to describe the *energy* requirements of biological systems.

These proposed carbon and oxygen parameters are made most attractive by the recent development of analytical instruments which provide the capability of determining, within a few minutes, the carbon content of both water and gas samples and the oxygen demand of water samples. It is also possible to distinguish between the organic and inorganic fractions of carbon present in both water and gases and, to a limited extent, between the dissolved and suspended carbon fractions in water.

Unit operations

In summary, I propose that *carbon* parameters be used to describe the food and culture content of microbiological systems and change in total oxygen demand (Δ TOD) be used to describe the energy requirements of those same systems. This approach is not proposed as a panacea to describe all aspects of biological reactions because many facets will require supplemental information. But the approach would assist in the breakdown of the biological treatment process into a series of describable unit operations which are amenable to material balances and more precise descriptions of unit rates. This concept will also provide a common basis for describing all biological systems, whether aerobic, anaerobic, or photosynthetic. Another important advantage is that analyses are made directly on the system being studied and do not involve setting up a secondary rate-limited system such as the BOD bottle.

First, a simplified carbon nomenclature is needed to describe the many forms in which carbon can be present. The following nomenclature is suggested for three-phase systems:

Liquid phase:
DOC—Dissolved organic carbon
DIC—Dissolved inorganic carbon

Solid phase:
SOC—Suspended organic carbon
SIC—Suspended inorganic carbon

Gas phase:
GOC—Gas organic carbon
GIC—Gas inorganic carbon

This nomenclature divides the carbon content of each phase on the basis of organic and inorganic carbon. Inorganic carbon is defined as carbon dioxide, or any carbon which will release carbon dioxide upon an acidification, such as CO_3^{2-} or HO_3^- in the liquid phase, or precipitate inorganic salts such as $CaCO_3$ in the solid phase. Organic carbon is defined as any carbon which does not fit the definition for inorganic carbon in any of the three phases. This definition for organic carbon is not entirely accurate, and there will be some exceptional cases which will need refinement, but the definition will be suitable for most applications.

Total oxygen demand (TOD) as used here refers to the oxygen demand of the whole aqueous sample. The net change in oxygen demand, therefore, includes dissolved and suspended reductants in the aqueous phase.

Use of carbon and oxygen demand parameters can provide two gigantic steps forward in pollution control technology:

• Analytical time is reduced from days to minutes, and

• It is possible to make both materials and energy balances.

Five days are required to run a standard BOD test, and a full working day to run a standard gravimetric test for suspended solids. No materials or energy balance is possible with the BOD test. With carbon and TOD parameters, on the other hand, analyses can be completed within minutes. The importance of reduced analytical time is obvious in that current, rather than historical, information can be obtained on a dynamic system. The ability to obtain materials and energy balances is basic to chemical engineering concepts and simply constitutes application of the laws of conservation of matter and energy.

Care must be taken in application of both carbon and TOD parameters because their use will vary with the system being studied. For instance, DOC may be the food source, SOC the culture, and SOC and GIC the end products in one system, while GIC or DIC may be the food source, SOC the culture, and SOC and DOC the end products in another system. The first reaction is typical of the aerobic bacterial

Obtaining a carbon balance on biological systems
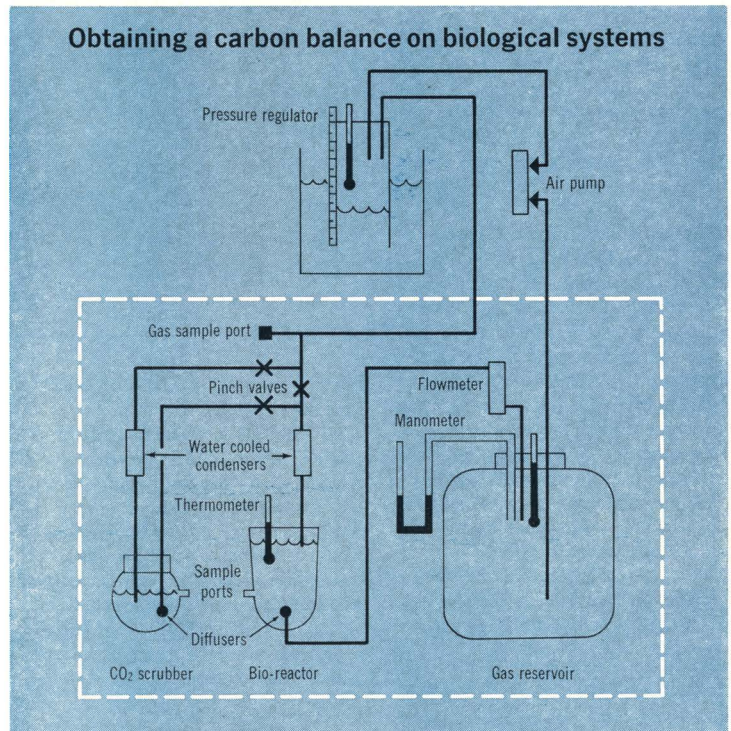
This experimental apparatus was used to study the parameters of biological systems. The system was adjusted to barometric pressure by raising or lowering the calibrated cylinder until the water levels matched; the incubator system (*dotted line*) was set at 27°C. ± 1°. Component volumes were as follows: bioreactor, 2380 ml.; gas reservoir, 20,710 ml.; tubing and condenser, 490 ml.; pressure regulator, 1640–3000 ml.; and CO_2 scrubber, 1140 ml. Culture substrate was made up from 625 mg. of ammonium phosphate and 180 mg. of glucose (as carbon) added to 2000 ml. of tap water. The sewage seed culture was one that had been acclimated to glucose, and 1 ml. was added at zero time to 1890 ml. of substrate in the reactor. Initial oxygen demand was 496 mg., and the initial oxygen available in the system was 7100 mg.

assimilation of phenol and the second system is typical of the photosynthesis reaction in algae growth. The energy requirement is represented by the decrease in TOD in the first case and by the increase in TOD in the second case.

Carbon balance

We recently made a study to determine whether it was actually possible to develop a materials balance on carbon in a three-phase, batch, biological system using instrumentation now available on the market. The system studied was the bacterial conversion of a pure substrate, glucose, to

bacterial cells and carbon dioxide, represented simply by:

$$DOC \xrightarrow{\text{bacteria}} SOC + GIC$$
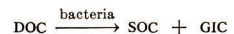
The experimental apparatus was a completely mixed bioreactor closed up with a recirculating gas (air) system. Components of the gas system included a gas pump, gas reservoir, a sparger in the reactor, condenser, and a device to maintain the system at barometric pressure and compensate for sample volume losses. This device assisted in the careful attention to the gas laws that were required.

If we exclude experimental procedures and details, it should be noted

that the greatest experimental problems were modification of the carbon analyzer instrument and development of analytical techniques. The test for chemical oxen demand (COD) was used for the energy parameter because a TOD analyzer was not available. Use of COD required larger sample volumes than would have been necessary with TOD analyses. Sample volume losses were accounted for in both the carbon and the energy balances of the system.

The results of this experiment allowed us to follow the carbon phase changes as bacterial activity converted glucose to bacterial cells and carbon dioxide. The carbon dioxide produced was, in turn, stripped from the aqueous phase by the recirculating gas (air). At intervals, and at the end of the experiment, all of the initial carbon was accounted for, even though it had been completely redistributed among the three phases of the system. Thus, at any given time during the run, the mass distribution of carbon could be displayed on a carbon mass–time plot as the vertical scale distance between the boundaries of each carbon parameter.

Energy requirements for the carbon conversion were determined as a change in chemical oxygen demand in the reactor. We initially thought that this satisfaction of oxygen demand in the aqueous phase could be balanced by determining the volumetric loss of oxygen from the gas phase. This energy balance was not accomplished in the experiment, though, due to the apparent involvement of gases other than carbon dioxide and oxygen. The makeup of these gases was not defined. The energy balance was completed, however, by equating the change in oxygen demand for the system to the oxygen equivalent of the inorganic carbon (CO_2) produced during the experiment. This approach was held valid for the carbohydrate, glucose, which contains sufficient oxygen in the molecule to satisfy the demand of the hydrogen present. Thus, for our present purposes, we can assume that the oxygen uptake balanced the satisfaction of oxygen demand in the liquid–solid phases.

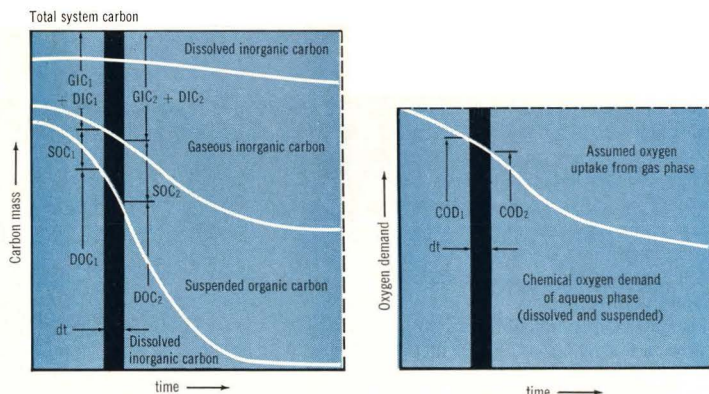Both stoichiometric and kinetic data can be obtained from carbon and oxygen demand progression charts. Stoichiometric data are developed by taking the differences in the carbon mass distribution and total oxygen de-

Total system carbon

mand over a set interval of reaction time in any reactor system—whether a lab reactor, treatment plant, or receiving stream. Stoichiometry of the reactions may then be expressed as in the accompanying table.

Kinetic data can also be determined using the unit change in respective carbon and oxygen demand parameters per unit time during any selected interval of time. Kinetic data may then be expressed in terms of carbon and oxygen demand parameters (see table).

Practical applications

Immediate application of this concept can be made to operation of treatment plants and monitoring of river systems. For instance, determination of DOC at intervals along the length of a conventional, plug flow, aeration basin will spot the point at which soluble organics have been exhausted or reduced to a constant. In most municipal plants this point may be surprisingly close to the basin inlet. Determination of SOC at the same points will provide a basis for calculating removal rate of DOC per SOC per unit time. By use of this rate, adjustment of return sludge (culture) may be made to proportion return SOC to raw waste DOC for the retention time of the basin. Adjustment should be made slowly and the unit rate checked continuously because the "apparent" activity and character of the culture will change as the system dynamics change in response to different loadings. In this manner, the loading situation which provides optimum results may be found and maintained because analytical response time is now minutes rather than days.

The practicality of this concept has

been proved for development of treatment plant design criteria on a variety of industrial waste waters. The rapidity with which determination can be made of bench scale or pilot-plant reactor kinetics is especially useful and provides a basis for control rather than just monitoring of the system. Boundary conditions are first imposed on the experimental setup to approximate those of the simulated treatment process, and response of the system to changes in variables can then be recorded. Important variables to consider include reaction temperature, culture acclimation to the conditions of hydraulic loading (solids separation rate) and mixing regime, food to culture loading, surface area to volume ratio (attached growth), carbon dioxide removal rate for pH control, and losses of volatile organics due to air stripping.

Equilibrium factor

The removal of CO_2 from a biological treatment system is often overlooked as a factor in the biological unit process. In dilute aqueous systems CO_2 is the major factor controlling pH which, in effect, becomes a measure of the equilibrium between the rate of CO_2 production in the aqueous phase and the rate of CO_2 removal from it. Herein also lies the need for accurate separation in the carbon analysis of DOC and DIC and the fallacy of assuming a constant DIC in a biological system.

The potential which the carbon and TOD analyzers offer has not yet been touched. Unfortunately, of the half dozen instruments now on the market, there is not one which is adequate at all for field use or even for laboratory

These two plots (opposite page) illustrate the development of parameters of a biological system for a given time interval dt. Stoichiometry for the time interval is as follows:

Item	Parameter	Units
Culture growth	$\Delta SOC = SOC_2 - SOC_1$	mg. or mg./liter as C
Substrate removed	$\Delta DOC = DOC_2 - DOC_1$	mg. or mg./liter as C
Yield	$\dfrac{\Delta SOC}{\Delta DOC}$	mg./mg.
Energy required	$\Delta COD = COD_2 - COD_1$	mg. of O_2
CO_2 produced	$\Delta GIC + \Delta DIC = (GIC_2 - GIC_1) + (DIC_2 - DIC_1)$	mg. of CO_2 as C

Using these stoichiometric data and the average SOC, as defined by $^1/_2(SOC_2 + SOC_1)$, the kinetics of the system can be developed as follows:

Unit removal rate	$\dfrac{\Delta DOC}{\text{Av. SOC dt.}}$	Unit oxygen uptake rate	$\dfrac{\Delta COD}{\text{Av. SOC dt.}}$
Growth rate	$\dfrac{\Delta SOC}{\text{Av. SOC dt.}}$	Unit CO_2 production rate	$\dfrac{\Delta GIC + \Delta DIC}{\text{Av. SOC dt.}}$

use without some modification. A description of modifications made to one commercial instrument has been published. Briefly, these modifications include:

• Reorientation and redesign of the "total carbon" combustion tube.

• Redesign of the injection port and carrier gas inlet to the "total carbon" combustion tube.

• Installation of an "acid-pool" type reactor system for inorganic carbon determination. Initially, a Van Hall-Stenger inorganic system was installed but was found to be limited by both diffusion and heat transfer.

• Addition of a manual switching arrangement for transfer of either the "total" or "inorganic" carbon systems into the detector cell circuit.

• Provision of an electrical interlock to indicate which system was in service and to reverse recorder polarity so the "total" carbon was recorded from left to right and "inorganic" carbon recorded from right to left.

These changes resulted in a significant improvement of the accuracy and precision of the instrument for the measurement of DOC, DIC, GOC, and GIC. However, the measurement of suspended carbon as SOC and SIC is not yet reliable because of the limitation of injected sample size in these instruments. It is just not possible to obtain representative samples of suspended solids content in the 20- to 40-microliter aliquots used by most carbon and TOD instruments. Homogenization of larger samples to reduce solids size and improve sampling reliability does not overcome this difficulty and, in fact, may increase the error which results from loss of volatiles in the homogenization step.

Volatile problems

Other problems, which have not been widely recognized, arise from the use of vacuum filtration and acidification with stripping by air or nitrogen as sample pretreatment steps. Volatile organics are lost in both of those steps and up to half of the original DIC can be removed by vacuum filtration as CO_2 is removed from the CO_2–HCO_3^{2-}–CO_3^{2-} equilibria of the sample. Since analytical differences (between "inorganic" and "total" analyses and between analyses of "whole" and "filtered" sample aliquots) are used to identify the four carbon forms —DOC, DIC, SOC, and SIC—any unknown losses of carbon in sample pretreatment steps will introduce an error in the determination of more than one parameter.

Careful use of pressure filtering methods eliminates the losses due to vacuum filtration; and the "acid pool" or similar reactor systems for direct analysis of inorganic carbon eliminate the need for acidification and nitrogen stripping. However, the suspended solids problem still remains, and until this analytical problem is solved the application of these rapid instrumental techniques will be severely limited. Change in COD can be substituted for TOD as the energy parameter until TOD instrumentation has been improved sufficiently to provide accurate analyses.

It is anticipated that adequate instrumentation will become available when demand for it is established. This demand will be established by chemists and chemical engineers who understand unit process engineering concepts and desire more rapid and definitive analysis than provided by

such tests as BOD and mixed liquor volatile suspended solids. Waste treatment can be a science rather than an art, and there is a great need in this field for people whose thinking is process oriented.

Additional Reading

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Leland L. Hiser is manager of water conservation research at Southwest Research Institute where he is supervising research on the detection and treatment of various industrial wastes. Mr. Hiser has a B.S. in mining engineering from the University of Arizona (1949) and an M.S. in environmental engineering from Rice (1963).

CALGON PATENTS CHEMICAL / PHYSICAL PROCESS FOR WASTEWATER TREATMENT

Polymer/Carbon System Can Produce Secondary or Tertiary Quality Water

Calgon Corporation has received a patent on its wastewater treatment process utilizing water-soluble polymers and other flocculants and granular activated carbon in a two-step sequence for treatment of municipal and industrial wastewaters.

Theodore M. Welton, Calgon president, said the company first announced the clarification/adsorption process development in February, 1967, and described it as "one of the most significant technological advances in sewage and wastewater treatment in the last 40 years."

Calgon says its process offers meaningful economic and operating advantages over conventional biological treatment. The company says its prime advantages are:

1. Capital costs are approximately 16 per cent less for secondary levels of BOD removal and 40 per cent less for tertiary treatment.

2. Capability to remove 90 to 95 per cent of organic pollutants including pesticides, phenols, dyes, polyols, TNT and other organics.

3. Land requirements are 85 per cent less.

"Lower land and capital costs mean that we can build more clarification/adsorption sewage treatment plants for the same amount of money. In effect, we can build almost 12 Calgon process plants for every 10 conventional secondary biological plants," Mr. Welton said.

Calgon says an even more important factor is that its process can provide consistent 90 to 95 per cent removal of BOD and suspended solids by simple operating changes such as more frequent reactivation of the granular carbon as compared with irregular removals of 90 per cent at best in biological plants.

"This means," Mr. Welton said, "that when consistent 90 per cent or higher removal of organic pollutants is mandated, a biological plant will have to be supplemented with a process such as granular carbon adsorption at additional capital and operating costs. It

appears more logical for financially hard-pressed communities to accomplish this objective in one step and at a single lower cost with clarification/adsorption treatment than in two steps, i.e. secondary biological plus adsorption later and at considerably higher costs."

Calgon says, too, that unlike a biological plant, its process is unaffected by toxic chemicals or by sudden changes in pH resulting from shock loads of acids or alkalies.

"In a biological system, pesticides, herbicides, some phenols and other toxic organics kill the microorganisms with the result that the toxic materials and some of the sewage organics pass through the plant virtually untreated," Mr. Welton said. "And since a biological plant has a high sensitivity to changes in pH, strong acids or alkalies can reduce its effectiveness."

He said this cannot happen in a clarification/adsorption plant.

"Since carbon adsorption is a physical phenomenon rather than biological, a carbon system is unaffected by sudden changes in pH and by toxic wastes. This safety factor is inherent in this patented process," he said.

Calgon says, too, that phosphate removal can be accomplished in its process with the use of precipitating chemicals such as lime or metal salts in the clarification step.

An additional advantage is that the new process reduces the sludge handling problem associated with a secondary biological treatment plant. Unlike a biological system in which microorganisms are constantly dying and producing solids, a carbon system adsorbs the organic materials in the pores of the carbon granules. These organics are then burned off at high temperatures when the carbon is thermally reactivated and purified for reuse.

Calgon also says that its system is esthetically acceptable since the odor problems associated with biological systems are nonexistent as a result of the elimination of secondary sludge. This makes possible the location of clarification/adsorption plants in urban areas.

Circle No. 12 on Readers' Service Card

Inventors of the process are Donald G. Hager, marketing coordinator for environmental products and services in the Water Management Division, and Ronald S. Joyce, research supervisor in the Pittsburgh Activated Carbon Division.

U. S. Patent 3,455,820 summarizes the process in these words:

"The present invention comprises treating raw sewage with a flocculant to cause separation of solids from the liquid, separating the effluent from the flocculated solids, passing the effluent through at least one bed of activated carbon, and periodically backwashing and regenerating the activated carbon."

The inventors state that granular carbon with a surface area of 300 to 1500 square meters per gram and a minimum mesh size of 50 is preferred. A carbon granule of mesh size 50 is comparable in size to the new freeze-dried coffee grains. One pound of this size granule, because of its intricate pore structure, has a surface area of 125 acres. Surface area is a significant factor because adsorption is a surface phenomenon in which molecules of organic materials adhere to the carbon.

Commenting on the process, Hager said regeneration or reactivation of the granular carbon is a key factor since reactivation in high temperature furnaces purifies the carbon for repeated reuse. Carbon losses in such a system average approximately five per cent for each reactivation cycle, he said.

The patent further states that either organic or inorganic flocculants can be used in the clarification step and that solids content of the clarified sewage must be reduced below 100 ppm to assure efficient operation of the granular carbon.

Further information on the Calgon process can be obtained by contacting Mr. Welton at Calgon Center, P. O. Box 1346, Pittsburgh, Pa. 15230. Telephone (412) 923-2345.

Calgon Corporation is a subsidiary of Merck & Co., Inc., the pharmaceutical-chemical manufacturer located in Rahway, New Jersey.

Mechanisms of Formation of Sulfur Oxides in Combustion

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■ The chemistry of sulfur oxidation processes is reviewed with respect to the kinetics and mechanisms of the various processes involved. Sulfur, hydrogen sulfide, carbon disulfide, methyl sulfide, and methyl mercaptan oxidation processes are examined. Detailed examination of the kinetics and mechanism of hydrogen sulfide oxidation is made based on slow reaction, fast (explosion) reaction, flash photolysis, and flame microstructure studies of hydrogen sulfide–oxygen systems. Special attention is given to the role of the lower oxides, SO and S_2O, in developing the mechanisms of SO_2 formation. The inhibiting effect of SO_2 on a number of combustion processes and the homogeneous formation and depletion of SO_3 in flames *via* the reaction of O atoms with SO_2 and SO_3 are also reviewed.

As with so many other factors in an ever-expanding society, SO_2 emissions from combustion sources, unless checked in the near future, will be increasing to serious proportions. Emissions of SO_2 are estimated currently at 22 million tons per year with the ominous forecast of 42 million tons by 1980. The major question seems: What can the air pollution engineer do about this? It is obvious that essentially all the sulfur in oil or coal will leave the stack as SO_2, with 1 to 2% showing up as SO_3. Two paths toward solving this problem are to remove the sulfur before combustion and to remove the SO_2 from the flue gases. Methods for desulfurizing oil by catalyzed hydrogenation processes and for removing some of the pyrites mechanically from coal are available. Costs for desulfurizing residual fuel, unfortunately, are high, ranging upward from about 50 cents per barrel. Removing sulfur from coal by separating pyrites from the fuel is limited generally by the size of the pyrites particles in the coal and because pyrited sulfur usually makes up only about half of the sulfur. The remaining organic sulfur cannot be removed short of gasifying the coal and cleaning up the resulting flue gas.

Methods for removing SO_2 by adsorption and reaction processes are also available and are currently being studied. One of the most promising of these economically is the injection of pulverized limestone or dolomite into hot flue gases, preferably just beyond the combustion zone, where the flue gases are hot enough to calcine the stone almost instantaneously, yet not so hot as to allow the lime or magnesia to react with the fuel ash. One of the problems here is the relative rate of reaction of the calcined stone with SO_2 and SO_3, or indeed with other sulfur oxides present momentarily at least in hot flue gas.

Perhaps other systems than desulfurizing fuel or cleaning up flue gases can be devised for decreasing the emission of objectionable sulfur oxides into the atmosphere. A third method might be whereby the reactions of sulfur during combustion would be controlled or modified so as to end up with innocuous products. Only a complete understanding of the many ways in which sulfur reacts with fuel constituents and oxygen during the burning process will disclose whether there are any reasonable hopes along these lines.

This paper details the manner in which sulfur forms a series of compounds with oxygen before, during, and after combustion, and the many interrelated factors that influence the occurrence of sulfur oxides in flue gases. Covering the most significant developments over the past 40 years, it provides a background for considering further efforts in the years ahead.

As much as we understand the phenomena of combustion today—especially of hydrocarbon combustion—the knowledge of sulfur oxidation processes during combustion is rather limited (see Urone and Schroeder, 1969). The purpose of this paper is to review some of the authors' and others' activities in this area and evaluate what is known of sulfur oxidation processes.

H_2S Oxidation

Flame Speed and Autoignition Limits. One of the most commonly studied sulfur-rich fuels is hydrogen sulfide, a gas, which at room temperature is easily ignited and stabilized in various flame geometries. The flame speed (Chamberlin and Clarke, 1928) and the autoignition limits (Jost, 1946) of H_2S–air mixtures are shown in Table I. The variation of flame speed with H_2S concentration is similar to hydrocarbon flames, and the flame speeds are comparable to hydrocarbon flame speeds, increasing to a maximum near the stoichiometric concentration (11.8% H_2S). The maximum flame speed occurs slightly on the lean side, suggesting the possibility of some decomposition in the preflame zone. The autoignition temperature reaches a minimum at about the stoichiometric mixture.

Coward and Jones (1931) report lower and upper flammability limits for H_2S–air as: lower limit, 4.3% H_2S; upper limit, approximately 45%.

Table I. The Flame Speed and Autoignition Limits of H₂S–Air Mixtures

Flame speed[a]		Autoignition limits[b]	
H₂S (%)	Flame, speed (cm./sec.)	H₂S (%)	Limit (° C.)
7.5	16.0	1	373
8.0	40.1	3	335
8.9	45.8	8	304
9.0	46.5	12	290
9.5	48.0	19.9	315
10.0	49.5	27	341
12.2	48.0	40	400
12.5	40.1	60	487
16.2	26.4		
20.0	24.0		

[a] Chamberlin and Clarke (1928).
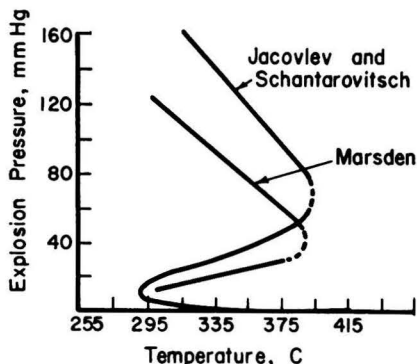[b] Jost (1946).

Figure 1. Explosion limits in stoichiometric H₂S/O₂ mixtures (Jacovlev and Schantarovitsch, 1937; Marsden, 1963)

Figure 2. The formation of (SO)₂ (Emanuel, 1944)

Preexplosion Studies. H₂S exhibits a characteristic three-explosion limit curve. Figure 1 shows the limit curves for stoichiometric H₂S–O₂ mixtures (Jacovlev and Schantarovitsch, 1937; Marsden, 1963). In the peninsula and in the third explosion limit region, explosion occurs after an induction period of several seconds. During this period, slow reactions prevail. Both sets of curves represent limit conditions for the same size vessels. Marsden suggests that the differences in the two curves may represent some nonuniformity in the temperature of the reaction vessel.

Farkas (1931) and Thompson and Kelland (1931) examined the temperatures and pressures under which the slow reaction converted to an explosion reaction. Farkas observed in the slow reaction region, 265° C. and 240 mm. Hg total pressure, that excess oxygen accelerates and excess H₂S retards the oxidation of H₂S. Thompson and Kelland expressed the rate of oxidation of H₂S in the manner

$$R_{-H_2S} = k \frac{(O_2)^y}{(H_2S)^x}$$

where $x = 0.14$ to 0.4 and $y = 1.2$ to 1.8. The activation energy for the process was determined to be approximately 18,000 calories per mole.

Taylor and Livingston (1931) carried out an Arrhenius analysis of the minimum explosion pressure of H₂S–O₂ mixtures. They recorded explosion pressures in the range 60 to 160 mm. Hg and obtained an activation energy of 17,180 calories per mole, in good agreement with the results of Farkas and of Thompson and Kelland. The chain character of these slow reactions is illustrated by induction periods, of the order of 30 to 120 sec., noted before explosion.

The chain character of the slow oxidation process for H₂S is also borne out in the studies of Emanuel and co-workers (1940) who followed the induction period of H₂S oxidation at 270° C. By observing simultaneously the pressure change in the system and the absorption spectrum in the ultraviolet region (2490 to 3400 Å), Emanuel obtains the curves shown in Figure 2. If H₂S were oxidized directly according to the equation of $H_2S + {}^3/_2 O_2 = H_2O + SO_2$, the decrease in pressure would occur immediately. As noted in the figure, however, for 27 sec. essentially no change in pressure occurs. During this period SO formation reaches its maximum rate, and, shortly after reaching its maximum concentration, the SO appears to decrease at a fairly rapid, constant rate.
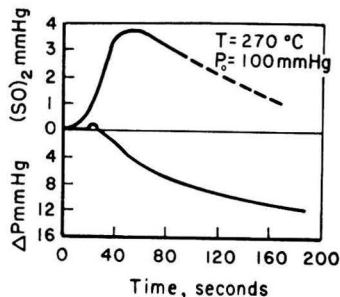
At the end of the induction period, a slight pressure rise is sometimes observed. As Emanuel points out in a later paper (Emanuel, 1944), this pressure rise is difficult to duplicate. Closer examination of the induction period often shows a very slight rise in pressure during this period preceding the well defined change when it occurs. From an Arrhenius analysis of the induction period preceding the slow reaction, Emanuel obtains the expression

$$tP_0^{1.3}e^{-20,000/RT} = \text{const.}$$

This equation agrees well with the expression obtained by Farkas for the induction period preceding explosion:

$$tP_0^{1.4}e^{-18,000/RT} = \text{const.}$$

Emanuel concludes the induction period reaction is

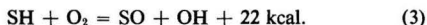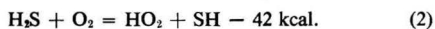$$H_2S + O_2 = H_2O + SO + 44,000 \text{ cal.} \qquad (1)$$
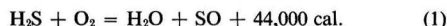
A complete explanation of the pressure rise is still not evident. While the dimerization of SO to S₂O₂ is exothermic, ultimately, as S₂O₂ is transformed to SO₂, pressure decreases. There is insufficient evidence at the present time to relate the dimerization process directly to the pressure rise at the end of the induction period.

The similarity in activation energies (17–20 kcal. per mole) noted by Farkas, Thompson and Kelland, Taylor and Livingston, and Emanuel is interesting. At the time of these studies, detailed mechanistic analyses were unavailable. Since the late 1930's and early 1940's, however, some detailed kinetics and mechanistic analyses have been carried out which help

present a clearer picture of the slow reactions leading to explosion.

Emanuel's identification of SO and the general recognition of a pronounced induction period suggest the following series of reaction steps:

$$H_2S + O_2 = HO_2 + SH - 42 \text{ kcal.} \tag{2}$$

$$SH + O_2 = SO + OH + 22 \text{ kcal.} \tag{3}$$

$$OH + HO_2 = H_2O + O_2 + 72 \text{ kcal.} \tag{4}$$

(There is some question as to the identity of the product SO as SO or S_2O. This is discussed further under a later section entitled *The Lower Sulfur Oxides*.) Summing these steps leads to

$$H_2S + O_2 = H_2O + SO + 52 \text{ kcal.} \tag{1}$$
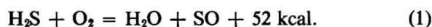
in fair agreement with Emanuel's suggestion that the formation of SO is exothermic by 44 kcal. per mole. If the three steps above are assumed as the primary preexplosion steps, then the OH and HO_2 radical buildup can occur by the first two steps with a minimum activation energy of about 20 kcal. per mole. Furthermore, the radical–radical reaction shown in Equation 4 would be expected to have nearly zero activation energy, giving a minimum overall activation energy of about 19 to 20 kcal. for the three-step process. This value is in good agreement with the experimentally derived activation energies in proceeding from the slow reaction to explosion reaction. By use of this simplified analysis, the induction period is explained as the period prior to attaining a critical concentration of OH and HO_2 radicals.

H_2S Oxidation Kinetics. Studies of the mechanism of H_2S oxidation reactions have been conducted by a number of investigators. Norrish and Zeelenberg (1957) made a detailed study of the chain reaction processes in the oxidation of H_2S using the flash photolysis technique. Levy and Merryman (1965a, 1967) applied the flame microstructure technique to derive the kinetics and mechanisms of some of the high temperature oxidation processes, while Bradley and Dobson (1967) studied the high temperature oxidation of H_2S in shock waves. McGarvey and McGrath (1964), using the flash photolysis technique, and Marsden (1963), employing mass spectrometric techniques, have identified and further confirmed the presence of several intermediates in the H_2S oxidation mechanism.

Flash Photolysis Studies

Norrish and Zeelenberg's studies were carried out at low pressures. The reaction vessel, about 50-cm. long, was flashed with up to 3000 J. of radiant energy. Spectra were obtained with a 350-J. spectroscopic flash at various times after the incident flash.

On flashing H_2S, Norrish and Zeelenberg noted the photochemical dissociation of H_2S to yield SH radicals. With mixtures of H_2S and O_2, a buildup of SH or OH is noted depending upon the O_2 concentration.

In lean mixtures, OH was more prominent as the initial appearance of SH was rapidly displaced by the appearance of OH. At later stages the OH disappeared as the SO_2 spectrum appeared; this stage was also accompanied by the emission of light. Although SO was not detected directly in their system, the S_2O_2 spectrum was noticed when H_2S–O_2 mixtures were flashed in the presence of excess inert gases. A characteristic of all the photolyses is the slow, delayed appearance of SO_2. On the basis of these results, Norrish and Zeelenberg present a mechanism for the oxidation of H_2S, much of which is included in the flame studies discussed in the following section.

Flame Studies

The authors have used the flame microstructure technique to obtain specific rate data for some of the more important steps in the oxidation of H_2S in flames. Details of the flame microstructure procedure used have been described (Levy and Merryman, 1965a). In essence, a flat H_2S–O_2–N_2 flame is stabilized on a flat-flame burner, and stable species are removed from the regions below, in, and above the flame. These stable species are then led into a mass spectrometer or other analytical device for analysis. Composition profiles, in conjunction with temperature and velocity profiles through the flame, are used to develop the kinetics of the oxidation processes. A typical set of concentration profiles is shown in Figure 3, obtained for a $^1/_{10}$-atmosphere H_2S–O_2–N_2 flame. All the species shown here were identified in the spectrometer.

In addition to the stable species, the active intermediate SO was detected in the flame samples by two different methods—a direct mass spectrometric detection using appearance potential techniques, and an indirect method wherein SO and SO_2 were removed simultaneously from the flame, oxidized in peroxide solution, and the SO obtained by difference after comparing the SO + SO_2 profile with the mass spectrometrically measured SO_2 profile. Rate profiles are calculated from the latter SO profiles after taking into account the effects of diffusion on the flame species. Figure 4 illustrates a set of rate profiles, based on the data of Figure 3, for the formation and depletion of some of the H_2S flame components.

A mechanism predominantly from Norrish and Zeelenberg's photolytic studies and containing additional reactions consistent with Levy and Merryman's flame studies follows:
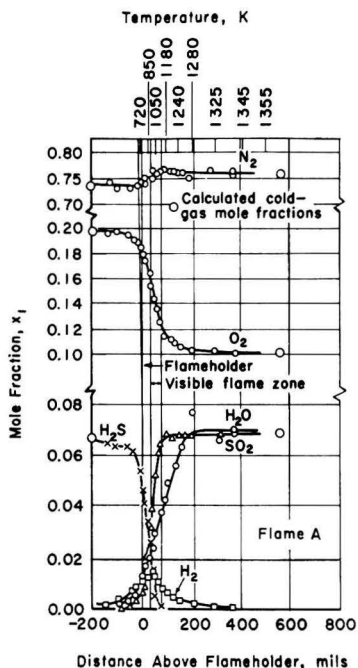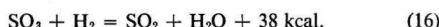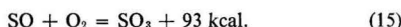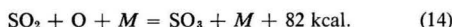
Figure 3. Composition profiles for H_2S-flame, pressure = 1/10 atmosphere (Merryman and Levy, 1967)

$$H_2S \rightarrow SH + H - 91 \text{ kcal.} \tag{5}$$

$$H_2S + O_2 = SH + HO_2 - 42 \text{ kcal.} \tag{2}$$

$$H + H_2S = SH + H_2 + 19 \text{ kcal.} \tag{6}$$

$$SH + O_2 = SO + OH + 22 \text{ kcal.} \tag{3}$$

$$OH + H_2S = H_2O + SH + 22 \text{ kcal.} \tag{7}$$

$$SO + O_2 = SO_2 + O + 18 \text{ kcal.} \tag{8}$$

$$O + H_2S = OH + SH + 19 \text{ kcal.} \tag{9}$$

$$SO + O \rightarrow SO_2^* \rightarrow SO_2 + hv \tag{10}$$

$$H + O_2 = OH + O - 16 \text{ kcal.} \tag{11}$$

$$O + H_2 = OH + H - 2 \text{ kcal.} \tag{12}$$

$$OH + H_2 = H_2O + H + 15 \text{ kcal.} \tag{13}$$

$$SO_2 + O + M = SO_3 + M + 82 \text{ kcal.} \tag{14}$$

$$SO + O_2 = SO_3 + 93 \text{ kcal.} \tag{15}$$

$$SO_3 + H_2 = SO_2 + H_2O + 38 \text{ kcal.} \tag{16}$$
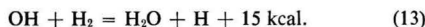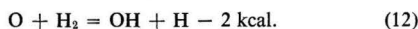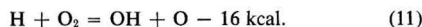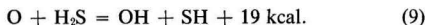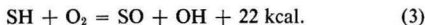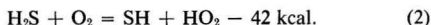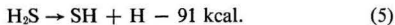
Radical–radical reactions are not shown in this mechanism; their contribution is of lesser importance. However, sulfur deposits were observed in nearly all of the flame studies made by the authors and, therefore, reactions of the type
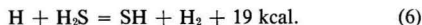
$$SH + SH = H_2S + S + 37.1 \text{ kcal.} \tag{17}$$

or

$$SH + SH \rightarrow S_2 + H_2 \tag{18}$$
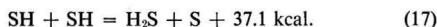
are not to be ignored.

There is some question as to the extent to which Steps 5 and 2 contribute to the initiation of the chain process. Undoubtedly Step 5 contributes to the photolytic oxidation of H₂S. Norrish and Zeelenberg suggest that the breaking of the H—SH bond will occur either thermally or by radical attack. Step 2, on the other hand, appears to be more consistent with a flame oxidation mechanism. It has been noted for example that preflame reactions occur during the combustion of H₂S with an overall activation energy of about 20 kcal. per mole increasing to 60 kcal. per mole in the visible flame zone—both energies too low for the thermal dissociation Step 5 to be significant (Merryman and Levy, 1967). Therefore, Step 2 is postulated as a major step in the consumption of H₂S, especially at the higher temperatures.

The subsequent oxidation of SH radical, produced from reactions such as 2, 6, etc., leads to the formation of SO, which plays an important role in the mechanism shown. As set out here, the primary reaction for the formation of SO₂ comes about by Step 8: $SO + O_2 = SO_2 + O$. Using this mechanism, the following rate constant is obtained for the production of SO₂

$$k = 5.2 \times 10^{14} \exp\left(-\frac{19{,}300}{RT}\right) \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$$

The activation energy appears consistent for a linear or four-centered-bond transition complex whereby an S—O bond is produced and an O—O bond is broken.

Bradley and Dobson (1967) have studied the oxidation of hydrogen sulfide in shock waves at temperatures from 1350° to 2450° K. Their results suggest the existence of a low and a high temperature mechanism in H₂S oxidation. At low temperatures (below 1560° K.) their data support the mechanism based on Reactions 3, 7–9. At higher temperatures, the
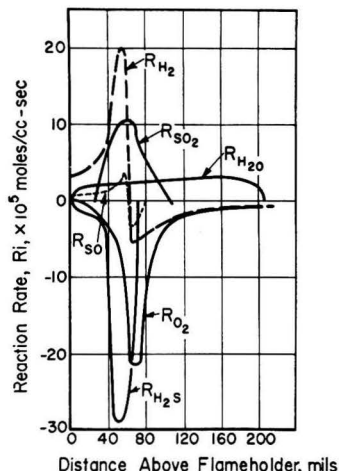

Figure 4. Rate profiles for H₂S flame (Merryman and Levy, 1967)

reaction $O + H_2S = H_2 + SO$ also appears to participate, leading to an increased rate of SO₂ formation.

The Lower Sulfur Oxides

The role assigned to SO and S₂O in the oxidation of H₂S to SO₂ has a moderate element of uncertainty. As pointed out earlier (Figure 4) the presence of SO in the high temperature flame oxidation of H₂S has been observed directly in recent flame probings. However, Norrish and Zeelenberg were unable to observe SO directly in the photolytic oxidation of H₂S. Norrish and Zeelenberg attempted to observe the absorption spectrum of SO by flashing S₂O₂ and SO₂. In each instance there was a complete temporary disappearance of the S₂O₂ or SO₂ spectrum, but no other spectrum appeared. They, therefore, postulate the existence of the SO by its emission spectrum in a flame; this spectrum however would have to result from a step such as

$$S + O = SO^* \tag{19}$$

since the step

$$SH + O_2 = SO + OH + 22 \text{ kcal.} \tag{3}$$
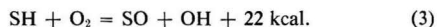
is not sufficiently exothermic to account for an excitation process.

The question has been raised in recent years whether SO, previously reported, is not really S₂O. Schenk and Steudel (1965) have recently reviewed some of the chemistry of SO and S₂O. Basic stability data reported in that study are presented in Table II. Based on the heat of decomposition, Schenk suggests that SO (like S₂) is present at appreciable concentration only at high temperatures and that SO behaves as a true biradical. Thus, it is suggested that SO is very reactive and decomposes immediately into sulfur or S₂O and SO₂. Hence, S₂O might be produced in the flame oxidation by

$$(SO)_2 + SO = S_2O + SO_2 \tag{20}$$

$$(SO)_2 + S_2 = 2S_2O \tag{21}$$
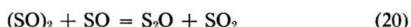
Marsden (1963) has observed S₂O mass spectrometrically. He has studied the oxidation of H₂S at temperatures of about 350° C. by allowing the reaction products to leak directly into the mass spectrometer. Marsden also observes an 8- to

12-sec. period of accelerating reaction where H_2 and S_2O are observed prior to explosion. Only during the explosion itself was SO evident. Although the formation of S_2O also appears conclusive, the manner in which S_2O is produced and whether it results from a rapid decomposition of SO have not yet been explained.

McGarvey and McGrath (1964), on the other hand, offer specific evidence for the SO radical in the photolytic oxidation of H_2S. Using the flash-photolysis technique, they observe a spectrum for SO in the ultraviolet region of 2400 to 1900 Å. They also note a delay in the appearance of the SO_2 spectrum. This delay is attributed to three possible reactions

$$SO + O_2 = SO_2 + O \qquad (8)$$

$$SO + O = SO_2* \qquad (22)$$

$$SO + O + M = SO_2 + M \qquad (23)$$
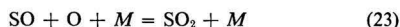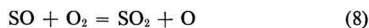
Kinetically, the first of these is most probable in any combustion process.

Azatyan, Gershenson, *et al.* (1969) have also identified the presence of SO in their ESR studies of rarified flames of H_2S, CS_2, COS, and sulfur vapors. They indicate a two-stage oxidation process in the consumption of H_2S. The first stage is characterized by the formation of SO_2, H_2O, H_2, and SO. The second stage involves the combustion of H_2. No direct evidence for the formation of S_2O is indicated.

Merryman and Levy (1970a) have recently completed a study of the formation of intermediates in H_2S, COS, and CH_3SH flames. By removing samples from the flames under molecular flow conditions and directing the samples into the analyzing unit of a quadruple mass spectrometer, the authors directly observed the formation and depletion of SO in the flames. Furthermore, S_2O formed in the H_2S flames under identical sampling conditions. The results are shown in Figure 5. The sequence of appearance of the lower sulfur oxides in the H_2S flame is shown to be S_2O followed by SO formation. If S_2O is forming prior to SO, it would follow the formation of S_2O in the flame is not the result of disproportionation of SO as suggested in Schenk's Equations 20 and 21. The path leading to S_2O formation is still uncertain, but S_2O might result from reactions of elemental sulfur with oxygen, $S_2 + O + M = S_2O + M$ or some similar reaction. Elemental sulfur, in relatively large quantities, was observed in the cooler preflame regions of the H_2S flames.

Oxidation of Sulfur

The frequent appearance of sulfur in H_2S oxidation studies would seem to indicate that it may be an important step in the oxidation mechanism. Semenov (1958), with reference to G. N. Ryabinin, has studied the vapor phase oxidation of sulfur at 100° to 150° C. and has shown that the oxidation reaction has all the attributes of a chain reaction. Specifically, the reaction is rapid, light is emitted, and sulfur–oxygen mixtures
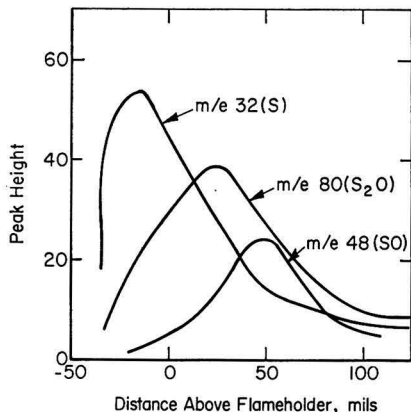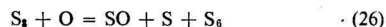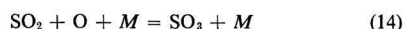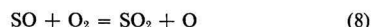

Figure 5. Intermediates in 1/10-atmosphere H_2S flame (Merryman and Levy, 1970)

exhibit the upper and lower limit phenomena of branched chain reaction. Semenov suggests the following initiation and branching reactions:

$$S_8 = S_7 + S \qquad (24)$$

$$S + O_2 = SO + O \qquad (25)$$

$$S_8 + O = SO + S + S_6 \qquad (26)$$

The products are SO_2 and SO_3 and are probably produced by the following reactions:

$$SO + O \rightarrow SO_2* \rightarrow SO_2 + hv \qquad (10)$$

$$SO + O_2 = SO_2 + O \qquad (8)$$

$$SO_2 + O_2 = SO_3 + O \qquad (27)$$

$$SO_2 + O + M = SO_3 + M \qquad (14)$$

Under these apparently favorable kinetic conditions, sulfur could well be an important intermediate product in the oxidation of H_2S to SO_2 and SO_3.

Carbon–Sulfur Oxidations

Oxidation reactions in compounds containing carbon and sulfur are of special interest since they come closest to the practical problem involved in burning coal containing appreciable amounts of sulfur. The systems are also of interest because they offer another route for unraveling the mechanism of sulfur oxidation processes.

The photooxidation of CS_2 and COS has been examined closely. Although photoinduced processes are not necessarily the same as thermal processes, some of these studies have helped in identifying the short-lived intermediate species that also exist in high temperature oxidation reactions. The spectra of SO_2, SO, and S_2O have definitely been identified in studies of Wright (1960) and Callear (1963). Wright, however, questions whether absorption noted between 2500 and 3400 Å should be attributed to SO or S_2O; based on the mass-spectrometric evidence of Myers and Meschi (1957) he assigns the absorption to S_2O. Wright does not disclaim the role of SO; on the contrary, based on flash photolysis, he points out that observations 1 msec. after the end of the flash do not indicate the presence of SO. He offers many possibilities for S_2O formation from SO:

$$SO + CS_2 = CS + S_2O \qquad (28)$$
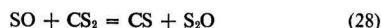
Table II. Bond Energies and Thermodynamic Data[a] for the Lower Oxides of Sulfur

	SO	S_2O
ΔH_0^0, kcal./mole	+1.6	−22.7
D_0, kcal./mole	(S—O) 123.5	(SS—O) 112.5
		(OS—S) 90.5
ΔH decomposition, kcal./mole	$SO \rightarrow 0.5 S + 0.5 SO_2 - 36.8$	$S_2O \rightarrow {}^3/_2 S + 0.5 SO_2 - 12.5$

[a] Schenk and Steudel (1965).

$$SO + S_2 = S_2O + S \tag{29}$$

$$SO + S = S_2O \tag{30}$$

$$SO + SO = S_2O + O \tag{31}$$
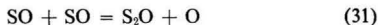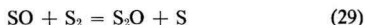
All of these steps are favored, although the first is probably most favored kinetically. Callear suggests that the rate of decay of SO ($v = 0$) was independent of oxygen pressure, while the vibrationally excited SO decayed very rapidly at high oxygen pressure.

Myerson, Taylor, *et al.* (1957) have conducted the most detailed study to date on the thermal oxidation of CS_2. This group studied the thermally initiated homogeneous explosion of CS_2–O_2 mixtures at temperatures of 190–300° C. by following the ultraviolet absorption spectra during and after the explosion. Evidence was obtained for the presence of CS, SO, SO_2, S_2O_2, S_2, and the superoxide ("isomer of SO_2") SOO. Myerson's group postulates that the explosion is initiated by a bimolecular process

$$CS_2 + O_2 = CS + SOO \tag{32}$$

similar to the initiation step proposed for the oxidation of H_2S

$$H_2S + O_2 = HO_2 + SH \tag{2}$$
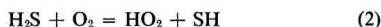
The superoxide, SOO, like some of the other sulfur oxides, is a rather elusive and interesting metastable product. Calculations indicate that SOO should be stable, but significantly less stable than SO_2. Myerson observed SOO by its continuous absorption in the ultraviolet, prior to the slow formation of SO_2 after explosion. Norrish and Oldershaw (1957) make a similar observation in their experiment where SO_2 is flashed in the ultraviolet. The SO_2 spectrum is noted to give way to a continuum and to reappear as the continuum disappears. McGarvey and McGrath (1964) assign a transient spectrum in the range 1840–1740 Å to SOO. Levy and Merryman (1965a,b) observed "excess" SO_2 values in mass-spectrometric analysis of SO_2 produced in the H_2S flame which may or may not have been associated with the superoxide. The studies of carbonyl sulfide flames by Levy and Merryman (1969) suggest the presence of SOO as an active intermediate in the oxidation of COS. The evidence, in general, has been fairly strong, but never completely firm, for recognizing the superoxide. In some way or other, however, SOO appears to be a precursor to SO_2 formation.

Myerson and his colleagues conclude their study yields strong evidence for SO as an important chain carrier. Myerson estimates the activation energy of the principal chain-propagating step

$$SO + O_2 = SO_2 + O \tag{8}$$
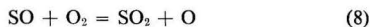
to be about 14 kcal. per mole. Data from Levy and Merryman's studies suggest an activation energy of 19 kcal. per mole for this step. It can be questioned here whether or not this is too high an activation energy for a principal chain-propagating step, recognizing, however, that this energy value is consistent with a four-centered-bond transition complex.

Harkness and Murray (1966a,b) have recently examined the slow oxidation of methyl mercaptan and methyl sulfide. These studies, although not detailed kinetic investigations, are useful. Both investigations were conducted at temperatures between 200° and 275° C. In each instance, gas–oxygen mixtures were combined in a reaction bulb, and oxidation rates were obtained as a function of the disappearance of reactants, appearance of products, or as a function of rate-of-pressure decrease.

In the mercaptan study, SO_2 was the principal product, other products being CH_4, CO, CO_2, H_2, HCHO, and CH_3OH. The nature of the products and the surface-conditioning effects observed indicate a chain process.

In the methyl sulfide study, explosions were observed at temperatures of 210° C. and above. Variable induction periods were observed prior to explosion. All explosions, even those with a slight excess of oxygen, yielded a light-colored deposit, presumably sulfur, on the walls. In the nonexplosive reactions, essentially all the methyl sulfide that reacted was oxidized to SO_2, while nearly all the carbon reacted appeared as CO.

Harkness and Murray observe distinct differences in the oxidations of methyl mercaptan and methyl sulfide. They suggest that the thiyl radical, CH_3S, may be important in the mercaptan oxidation and unimportant in the methyl sulfide oxidation. This conclusion is based on the assumption that initiation of the mercaptan oxidation is through

$$CH_3SH + O_2 = CH_3S + HO_2 \tag{33}$$

$$CH_3S + O_2 = CH_3 + SO_2 \tag{34}$$
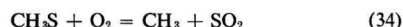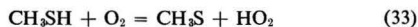
while the lack of any methane formation in the oxidation of methyl sulfide precludes such steps as the second one.
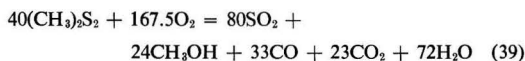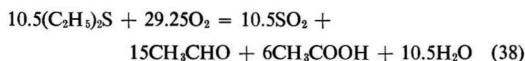
Cullis and Roselaar (1959a,b) have studied the gas-phase oxidation of dialkyl sulfides and dimethyl disulfide at temperatures of about 190° and 240° C., respectively. The reaction was followed manometrically in a closed system containing oxygen and the organic sulfide. The initial step in the oxidation processes is postulated to be the abstraction of a hydrogen atom from the organic residue. For the alkyl sulfides, the initial steps are given as

$$(CH_3)_2S + O_2 = CH_3SCH_2 + HO_2 \tag{35}$$

for dimethyl sulfide, and

$$(C_2H_5)_2S + O_2 = CH_3CH_2SCHCH_3 + HO_2 \tag{36}$$

for diethyl sulfide. A reaction similar to that for dimethyl sulfide is given for the first step in the oxidation of dimethyl disulfide. The experimental data suggest the following overall reactions for the oxidation of dimethyl sulfide, diethyl sulfide, and dimethyl disulfide, respectively:

$$(CH_3)_2S + 2.5O_2 = SO_2 + CH_3OH + CO + H_2O \tag{37}$$

$$10.5(C_2H_5)_2S + 29.25O_2 = 10.5SO_2 + 15CH_3CHO + 6CH_3COOH + 10.5H_2O \tag{38}$$

$$40(CH_3)_2S_2 + 167.5O_2 = 80SO_2 + 24CH_3OH + 33CO + 23CO_2 + 72H_2O \tag{39}$$

Sulfur dioxide appears to be the only major product common to all three oxidation processes. It has a pronounced inhibitive effect on the oxidation of dimethyl sulfide. For example, explosion in a mixture of diethyl sulfide (50-mm. pressure) and oxygen (100-mm. pressure), which occurs in about 3 sec. at 178° C., is completely inhibited upon the addition of 3.6 mm. of SO_2 to the mixture. Cullis and Roselaar suggest that the sulfide itself, rather than a chain carrier, is inhibited from oxidation by SO_2. This was partly because sulfur dioxide showed no inhibitive influence on the autooxidation of acetaldehyde, an intermediate product of diethyl sulfide oxidation. It is generally true, however, that SO_2 does exert an inhibiting effect on a number of combustion processes. The mechanism of this inhibition process is not especially well understood yet. Kurz (1956) has shown that the addition of

H$_2$S to various hydrocarbon fuel mixtures results in a marked reduction in flame stability. He attributes this inhibition effect to interactions of elemental sulfur with hydrocarbon fragments. More recent studies, however, suggest that SO$_2$ plays the major role in the inhibition mechanism and often conclude that the inhibiting influence is due to the reaction between SO$_2$ and O-atoms (Williams, 1963), and this may also be the case in the dialkyl sulfide studies above. Recently, however, Webster and Walsh (1965), in a study of the inhibiting effect of SO$_2$ in the H$_2$–O$_2$ system, suggest that under conditions of the second explosion limit, inhibition occurs by removal of H atoms

$$H + SO_2 + M = HSO_2 + M \qquad (40)$$

Cullis, Henson, et al. (1967) have studied some reaction systems containing SO$_2$ in decomposing hydrogen peroxide vapor and in reacting organic fuel mixtures. They observe that in reactive conditions up to 700° C. the rate of reaction of SO$_2$ with oxygen-containing radicals is negligible. They report no appreciable loss of SO$_2$ in separate systems containing H$_2$O$_2$, ethanol, ethane, or benzene, except when temperatures are momentarily increased above 700° C., as during an ignition reaction.

SO$_2$ formation from the dialkyl sulfides presumably arises from the oxidation of a thioaldehyde, $RCHS(R = H$ or $CH_3)$ formed as an intermediate product. Similarly, for dimethyl disulfide, the formation of CH$_2$S and the radical CH$_3$S as intermediates leads to the formation of SO$_2$. No significant amount of methane was found in the dialkyl sulfide oxidation studies which suggests that the CH$_3$S radical does not play a major role in these oxidation processes. These results are in agreement with those observed by Harkness and Murray (1966a).

The Oxidation of H$_2$S and SO with Ozone

The oxidation of sulfur compounds by ozone is of more concern to conditions in the troposphere and stratosphere than in the lower regions of the environment. Ozone is an important contaminant in the lower atmosphere, however, and does enter into numerous smog-producing reactions. In general, the oxidation of sulfur compounds by ozone is not a rapid reaction, but this does warrant some consideration.

The reaction between hydrogen sulfide and ozone was recently studied by Cadle and Ledford (1966). The kinetics of the reaction were followed in a flow reactor equipped with a photometer tube to measure the concentration of reactants and products. The experiments were carried out at atmospheric pressure in the temperature range 299° to 373° K.

From the infrared spectrum of the products, it was found that

$$H_2S + O_3 \rightarrow H_2O + SO_2 \qquad (41)$$
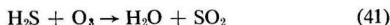
closely represents the stoichiometry of the overall oxidation process. However, the order of reaction with respect to hydrogen sulfide and to ozone was found to be about 0 and 1.5, respectively. The nearly zero-order dependence on hydrogen sulfide was attributed to H$_2$S adsorption on the reactor walls; the reaction was found to be at least partially heterogeneous. The 1.5 order with respect to ozone was not explained.

From the nature of the surface effects and orders of reaction, it is concluded that the rate-controlling step is not a simple bimolecular addition or hydrogen abstraction step. However, no detailed discussion of the mechanism involved was offered since the data were insufficient to establish conclusive results on the path of the reaction. An activation energy of
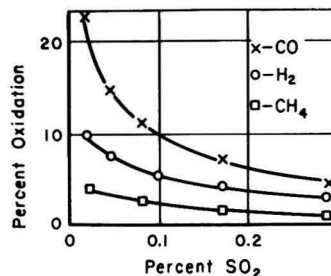

Figure 6. Oxidation of SO$_2$ in various flames (Dooley and Wittingham, 1946)

8300 cal. per mole was determined for the reaction, while the rate constant is given as

$$k = 2.5 \times 10^8 \exp(-8300/RT) \text{ cm.}^{1.5} \text{ mole}^{-0.5} \text{ sec.}^{-1}$$

Since SO$_2$ is one of the major products of the oxidation reaction, it would seem logical that the reaction between SO$_2$ and O$_3$ should also be considered. Cadle (1956) has shown, however, that this reaction is very slow. Therefore, it was assumed to be of minor importance in the H$_2$S–O$_3$ studies.

Halstead and Thrush (1966b) have recently reported on the chemiluminescent reaction between sulfur monoxide and ozone. These studies were carried out in a fast-flow system at pressures between 0.3 and 3.0 mm. Hg. The overall reaction is represented by:

$$SO + O_3 \rightarrow SO_2 + O_2 + 106.6 \text{ kcal./mole} \qquad (42)$$
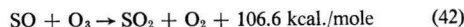
This rapid bimolecular reaction produced both ground-state products and electronically excited SO$_2$ molecules in the ^1B and $^3B_1$ states. In the case of the ground-state products, the rate constant for Reaction 42 was determined as $k = 1.5 \times 10^{12} \exp(-2100/RT)$ cm.^{3} mole^{-1} sec.$^{-1}$. For the electronically excited molecules, the rate constant was found to be $10^{11} \exp(-4200/RT)$ cm.^{3} mole^{-1} sec.$^{-1}$ for the ^1B state of SO$_2$, and $>3 \times 10^{10} \exp(-3900/RT)$ cm.^{3} mole^{-1} sec.$^{-1}$ for the $^3B_1$ state. Formation of electronically excited SO$_2$ here apparently involves a higher energy barrier than the formation of ground-state SO$_2$. The amount of heat released during the formation of electronically excited SO$_2$ and ground-state O$_2$ (no excited O$_2$ was found) is 21 kcal./mole for the ^1B SO$_2$ state and 35 kcal./mole for the $^3B_1$ state; these are considerably smaller values than the 106 kcal./mole for formation of ground-state SO$_2$.

Oxidation of SO$_2$ to SO$_3$

The occurrence of SO$_2$ in a system invariably is accompanied by detectable quantities of SO$_3$. In many situations the maximum level of SO$_3$ available is established thermodynamically. However, the rate of approach to equilibrium in a homogeneous SO$_2$–SO$_3$–air environment is slow. As a result, SO$_3$ will usually be observed at less-than-equilibrium levels in the atmosphere. In general, the SO$_3$ produced along with SO$_2$ in any combustion process will vary with the concentration of SO$_2$. Figure 6 illustrates this point (Dooley and Wittingham, 1946).

The early studies of the gas-phase oxidation of SO$_2$ to SO$_3$ were directed toward determining the equilibrium distribution of SO$_2$ and SO$_3$ at various temperatures in a gas mixture containing initially oxygen, sulfur dioxide, and a catalyst to increase the rate of oxidation. The overall reaction studied was:

$$SO_2 + 0.5O_2 \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} SO_3 + 22.6 \text{ kcal./mole} \qquad (43)$$
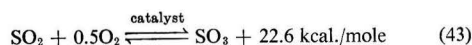
Several references to these equilibrium studies are found in a number of review articles, such as those of Hedley (1967), Pankhurst and Styles (1963), and Williams (1963), which treat the kinetics of SO_3 formation in combustion processes.

The kinetics of the approach to equilibrium under homogeneous conditions has received only limited attention, probably because the reaction proceeds at an extremely slow rate in the absence of a catalyst, even at temperatures above $800°$ C. Furthermore, the equilibrium data predict only very small quantities of SO_3 would exist in a gas mixture at $1000°$ to $1100°$ C. Thus, the region of kinetic studies is limited to the rather small temperature range of $800°$ to $1000°$ C.

Recently, in a paper by Cullis, Henson, *et al.* (1966), kinetic data are reported on the noncatalyzed gas-phase reaction between SO_2 and O_2. From these studies, the rate of formation of SO_3 in the absence of catalysts was found to be approximately 7.2×10^{-6} mole liter^{-1} min.$^{-1}$ at $950°$ C. Addition of N_2 or H_2O to the SO_2–O_2 mixture did not appear to change the rate of SO_3 formation. But, the addition of NO to the mixture resulted in a noticeable reaction rate at temperatures as low as $400°$ C.

In the noncatalyzed reaction, the rate-determining step is postulated to be the collisional activation of SO_2 molecules requiring 75 kcal./mole of energy. The addition of NO to the SO_2–O_2 mixture lowered the activation energy requirements to zero at high NO concentrations (10^{-3} to 10^{-4} mole per liter, $T < 900°$ C.) while at low NO concentrations (below 10^{-4} mole per liter) the activation energy was found to be about 25 kcal. per mole. The order of reaction with respect to NO drops from 2 at high NO concentrations to 1 at low NO concentrations. The difference in the kinetics is explained on the basis of competitive reactions postulated between SO_2 and NO_3 molecules as shown by the following reactions:

$$NO + O_2 = NO_3 \tag{44}$$

$$NO_3 + NO = 2NO_2 \tag{45}$$

$$NO_3 + SO_2 = NO_2 + SO_3 \tag{46}$$
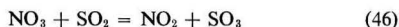
If we assume equilibrium is established in the first step at high NO concentrations, the second-order kinetics with respect to NO is observed as the second step becomes rate-determining. At low NO concentrations, the last step predominates.

Although SO_3 can be formed in the gas-phase reaction between SO_2 and O_2 at high temperatures and from the reaction of SO_2 with nitrogen oxides, neither reaction appears to be a major contributor to SO_3 formation in fuel-burning units. The major source of SO_3 in the gas stream appears to come from the homogeneous gas-phase reaction between sulfur dioxide and oxygen atoms as discussed below. No doubt some SO_3 can also be produced from the heterogeneously catalyzed oxidation of SO_2 on iron oxide surfaces, but substantial experimental data indicate that this type of reaction is unlikely to be a major source of SO_3 in combustion gases (Williams, 1963, Pankhurst and Styles, 1963, Jüntgen, 1963, Hedley, 1967). Catalyses on surfaces such as oxidized or V_2O_5-coated superheater elements in boiler furnaces undoubtedly contribute markedly to external corrosion processes, but these are highly localized conditions that do not radically affect the SO_3 levels in the bulk of the gas stream flowing through a boiler.

The reaction between sulfur dioxide and oxygen atoms has received attention in the past years. Dooley and Wittingham (1946), in their oxidation studies of SO_2 in flames, showed that the amount of flame-produced SO_3 increased in the order methane:hydrogen:carbon monoxide (Figure 6). This order

also happens to be the order the O-atom concentrations are observed to increase in these three flames (Gaydon, 1944). This strongly suggests that the oxidation of SO_2 in flames occurs by O-atom reaction.

Hedley (1962, 1963), using a kerosene-fired furnace and adding CS_2 to give 2% sulfur in the fuel, showed that higher-than-equilibrium values of SO_3 were obtained in the high temperature regions of his furnace. His results are illustrated in Figure 7. Since the molecular reaction between SO_2 and O_2 would not produce higher-than-equilibrium values of SO_3, Hedley proposed the following successive reactions to account for his observed results:

$$SO_2 + O \xrightarrow{k_1} SO_3^* \xrightarrow{k_2} SO_2 + 0.5O_2 \tag{47}$$

The $k_1 : k_2$ ratio is given as approximately 8. At the SO_2 concentrations encountered in Hedley's flames, the value of k_1 is calculated to be about 4.5×10^{13} cm.^{6} mole^{-2} sec.$^{-1}$ (maximum flame temperature $\sim 1800°$ K.). The value of k_1 derived from Dooley and Wittingham's SO_2 oxidation studies is about one order of magnitude less than Hedley's value. The reaction $SO_3 + O \rightarrow SO_2 + O_2$ is not suggested by Hedley's analysis. This reaction, a possibly important one in this regard, is discussed later.

Levy and Merryman (1965b) obtained SO_3 profiles showing the formation of SO_3 just above the visible flame zone. It is concluded from the nearly constant temperature and SO_3 concentrations observed in the post-flame probings, that the SO_3 was formed only from the reaction of SO_2 with O atoms, since if oxygen molecules were oxidizing the SO_2 to SO_3, the SO_3 concentration would continue to increase in the post-flame region. This conclusion is illustrated in the profile of Figure 8.
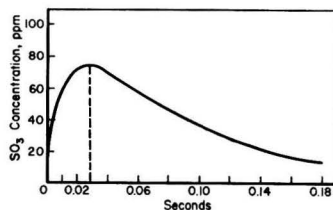

Figure 7. Variation of SO_3 concentration with time (Hedley, 1962)
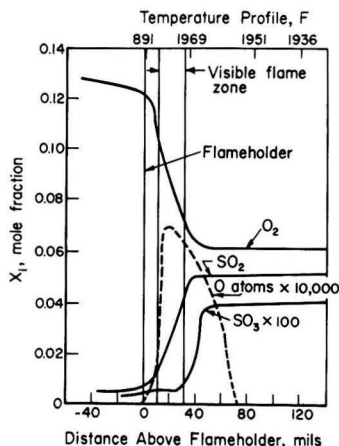

Figure 8. SO_3 formation in flame (Levy and Merryman, 1965b)

From steady-state assumptions, and assuming an activation energy of 6000 cal. per mole (more recent studies suggest 2500 cal. per mole for the activation energy) for the reaction $SO_2 + O + M \xrightarrow{k} SO_3 + M$, a value of k is calculated at 1.5×10^{15} cm.^{6} mole^{-2} sec.$^{-1}$ at 784° K. Mulcahy, Steven, et al. (1967) have studied the SO_2–O reaction at 300° K. using ESR spectrometry and have reported a value of $k = 2.4 \pm 0.15 \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$ for $M = Ar$. Values of k for $M = SO_2$ or O_2 are also reported. Halstead and Thrush (1966a) have also studied the SO_2–O reaction at 300° K. and report a value of $k = 4.7 \pm 0.8 \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$, $M = Ar$, in good agreement with Mulcahy's value. These values compare with the approximate values of Kaufman (1958), $k \cong 3 \times 10^{16}$ cm.^{6} mole^{-2} sec.$^{-1}$ at 295° K., and of Webster and Walsh (1965), $k = 1 \times 10^{16}$ cm.^{6} mole^{-2} sec.$^{-1}$ at 784° K. However, all of these k values are several orders of magnitude higher than those reported by Hedley or by Dooley and Wittingham.

Jüntgen (1963) and Fenimore and Jones (1965) have studied the SO_2–SO_3 equilibrium condition in flames. Fenimore and Jones added SO_2 to H_2–O_2 flames under H_2-lean and H_2-rich conditions. They found that SO_3 readily forms in the H_2-lean flames. The SO_3:SO_2 ratio in the lean flames was 0.014. This ratio is quite inconsistent with ratios derived from such equilibria as:

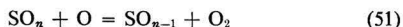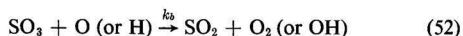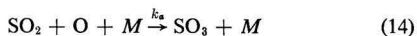| Reaction[a]	Ratio SO_3:SO_2
$SO_2 + 0.5O_2 \rightleftarrows SO_3$	0.0027
$SO_2 + O_2 \rightleftarrows SO_3 + O$	0.00001
$SO_2 + O + M \rightleftarrows SO_3 + M$	0.78

[a] Temperature = 1600° K.

To account for the discrepancy in ratios, Fenimore and Jones have referred to some earlier equilibria studies of Sugden and co-workers (1961). Sugden's group has suggested that equilibria exist in the hydrogen–sulfur system with the same characteristics of rapid equilibrium steps as the hydrogen–oxygen system:

$$H + O_2 = OH + O \qquad (11)$$

$$O + H_2 = OH + H \qquad (12)$$

$$OH + H_2 = H_2O + H \qquad (13)$$

$$H + S_2 = HS + S \qquad (48)$$

$$S + H_2 = HS + H \qquad (49)$$

$$HS + H_2 = H_2S + H \qquad (50)$$

Sugden also suggested the equilibrium

$$SO_n + O = SO_{n-1} + O_2 \qquad (51)$$

Fenimore and Jones have essentially extrapolated this equilibrium step to SO_3 and have applied the steps

$$SO_2 + O + M \xrightarrow{k_a} SO_3 + M \qquad (14)$$

$$SO_3 + O \text{ (or H)} \xrightarrow{k_b} SO_2 + O_2 \text{ (or OH)} \qquad (52)$$

to observed steady-state ratios of SO_3:SO_2 in lean flames. The driving force of this latter reaction prevents equilibrium from being attained and results in the observed nonequilibrium ratios. If we assume this reaction is valid and using Kaufman's rate constant value for the former step, a steady-state ratio of SO_3:SO_2 can be expressed by

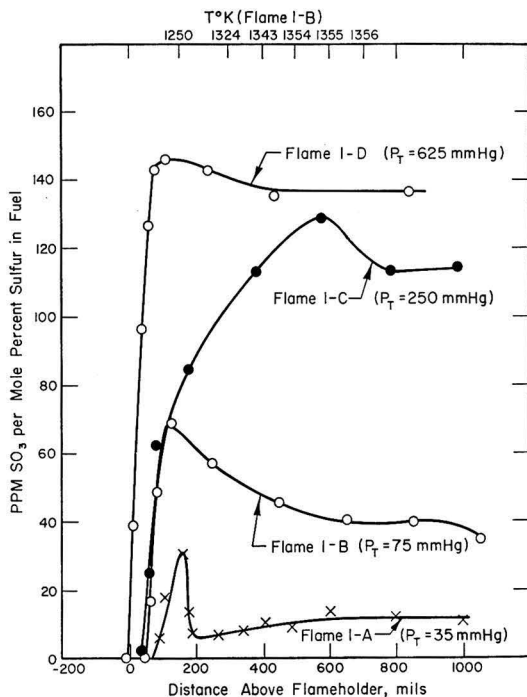$$\frac{SO_3}{SO_2} = \frac{k_a(O)(M)}{k_b[(O) + (H)]}$$

Figure 9. SO_3 profiles in H_2S flames (Merryman and Levy, 1970b)

where k_b is an average rate constant for the interaction of O or H with SO_3. Fenimore and Jones roughly determined the value of k_b to be 10^{12} cm.^{3} mole^{-1} sec.$^{-1}$ at approximately 1600° K.

Merryman and Levy (1970b) have studied the depletion of SO_3 in H_2S and COS flames. Data from the H_2S flame probings are shown in Figure 9. The increasing depletion of SO_3 with decreasing pressure is taken as evidence for the SO_3–O atom reaction since the lifetime of the O-atoms would increase with decreasing pressure. From the SO_3 studies, the rate constant expression, $k_b = 6.5 \times 10^{14} \exp^{-10,800/RT}$ cm.^{3} mole^{-1} sec.$^{-1}$, was obtained. Evaluating k_b at $T = 1600°$ K. gives $k_b = 3 \times 10^{13}$ cm.^{3} mole^{-1} sec.$^{-1}$, about an order of magnitude higher than that estimated by Fenimore and Jones (1965).

These k_b values are significantly higher than the rate constant determined by Hedley (1963) and by Nettleton and Sterling (1969) for the thermal decomposition of SO_3*: $k_2 \cong 4 \times 10^8$ cm.^{3} mole^{-1} sec.$^{-1}$ at about 1700° to 1800° K. Assuming these rate constant values are correct, it would appear that the depletion of flame-produced SO_3 occurs mostly by O or H attack rather than thermal decomposition. These are significant observations in that they present a reasonable explanation for the nonequilibrated system and for the commonly reported 1 to 2% oxidation of sulfur to SO_3 in combustion gases.

Conclusions

This review has pointed out the many areas where information on the oxidation of sulfur compounds is still lacking. Thus, to review briefly, the slow, preexplosion reactions of H_2S and O_2 appear to suggest a process whereby the partial oxidation product SO is produced. This is substantiated in

part by the energetics of various preexplosion studies and by some of the flame kinetics. On the other hand, the role of SO and S_2O in SO_2 formation has not been substantiated in an unqualified manner by any of the investigations to date. It can be stated that both species are precursors to SO_2 formation in H_2S flames, but their roles may differ in different flames. Then, on more tenuous grounds, there is the spectroscopic evidence for the superoxide of sulfur, SOO, as a precursor to SO_2 formation.

Understanding of the oxidation of the organic sulfur compounds, such as the mercaptans and the sulfides, is sketchy. The limited number of studies made have not included detailed studies of kinetics. Thus, different mechanisms are suggested, but here, too, the evidence is still fragmentary.

The homogeneous O-atom oxidation of SO_2 in combustion appears to be well affirmed. Kinetic data, however, are not clear; a spread of several orders of magnitude is evident in comparing the results of various workers.

Complexity of the reactions occurring in the oxidation of sulfur compounds is indicated by the many reasonable, but often contradictory, postulates developed over the past few decades. Now that sulfur oxides are being considered as major contributors to air pollution, research on the basic reactions leading to their formation will be accelerated. New laboratory tools, fresh experimental approaches, and inventive thinking will all lead to an even better understanding of the complicated fashion in which sulfur reacts with oxygen. Eventually, the remaining secrets in this involved system will yield to the combined attack of a great many researchers working in many technological disciplines.

Acknowledgment

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Simultaneous Removal of Fly Ash and SO₂ from Gas Streams by a Shaft-Filter-Sorber

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■ A shaft-filter-sorber has been shown to be an effective device for the simultaneous removal of SO₂ and fly ash from gas streams. A shaft-filter-sorber consists of a bed of slowly falling sorbent pebbles through which a gas stream to be cleaned passes horizontally. A number of tests that use alkalized alumina as sorbent have shown that complete SO₂ removal and 99+ % filtration efficiency are possible at gas mass velocities of 150 lb./hr. ft.² and dust loadings in excess of 3 grains per s.c.f. The SO₂ removal is predictable on the basis of static bed experiments, and a design curve based on this prediction is presented as a means of projecting removal efficiencies at higher gas velocities.

T he simultaneous removal of both dust and gaseous pollutants (SO₂, SO₃) from flue gas may be accomplished in many ways. Conceptually, such dual-purpose schemes could combine the steps of filtration with chemical reaction or sorption of the gaseous contaminants by hot solids. One specific way in which this combination may be effected is by use of a shaft-filter-sorber.

Basically, a shaft filter consists of a bed of slowly falling pebbles through which the gas stream to be filtered passes horizontally. Sulfur dioxide is removed by the pebble bed which consists of a material that picks up the SO₂, and any one of many solid sorbents can be used. This paper presents the results of experiments using alkalized alumina as the sorbent material.

Previous experiments have shown that the presence of fly ash in the inlet gas stream does not reduce the rate of SO₂ removal by alkalized alumina, nor does it have any other apparent harmful effect on the sorbent (Zahradnik, Toor, *et al.*, 1968). Experiments reported in this paper show that previously established rate models can be modified to describe the performance of a shaft-filter-sorber. Also, a number of experiments are reported which illustrate that high filtration efficiency and SO₂ removal capacity may be obtained in such a unit.

Shaft-Filter-Sorber Equipment

A Hoffman blower was used to move an air stream through a gate valve into the system. Two chromalox heaters (20 kW, 9 kW) were used to heat the gas stream to sorption temperature. After the air flowed through an orifice meter, SO₂ was added from an SO₂ cylinder. A precalibrated screw feeder added fly ash from a storage bin.

The shaft filter used is a square cross-section shaft, total length 8 ft.; the top 7 ft. serve as the storage area, the remaining 1 ft. is the actual filtering section. The cross-sec-
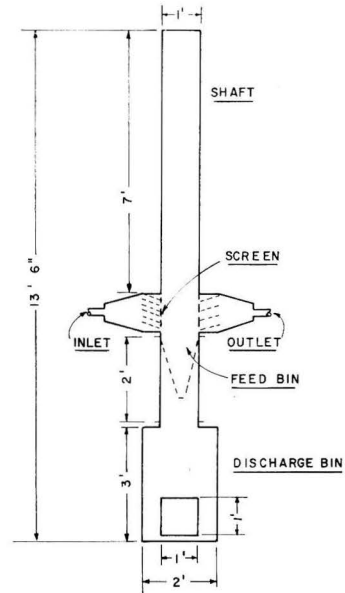

Figure 1. Shaft filter, front view

tional area is 1 ft.² The gas flows cross currently and the inlet and outlet sections are louvered to obtain a uniform distribution of flow. The shaft walls are carbon steel plates, ¹/₄-in. thick. A detailed drawing of the filter is illustrated in Figure 1.

The shaft was charged with filtering material at the beginning of a run, and the pebbles were removed through the lower part of the shaft by a precalibrated natural frequency vibrating feeder. This type of feeder provided a uniform solids flow rate independent of the static head, a very desirable characteristic.

The SO₂ concentration in the inlet and outlet gas was determined by standard iodometric titration. A vacuum pump was used to provide uniform pressure in the sampling lines. The pressure drop across the filter was measured by a U-tube manometer with mercury as manometric fluid.

SO₂ Sorption by a Moving Bed

The sorbent material used in the experiments was alkalized alumina, provided in various forms by the U.S. Bureau of Mines. To verify that this material behaves similarly to that observed by the Bureau and to establish specific reaction-rate parameters, the following experiment was performed. Sev-
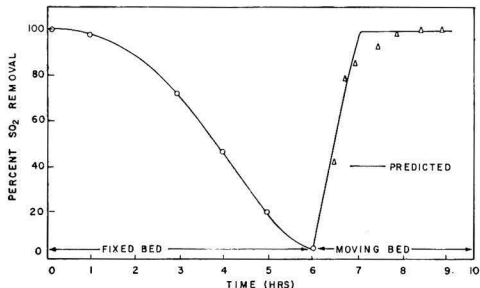
Figure 2. SO_2 removal vs. time for fixed and moving bed

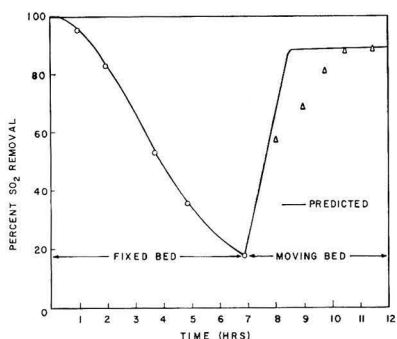Gas flow rate, 21.6 s.c.f.m.; inlet SO_2, 1.33%; solids rate, 53 lb./hr.

Figure 3. SO_2 removed vs. time for fixed and moving bed runs

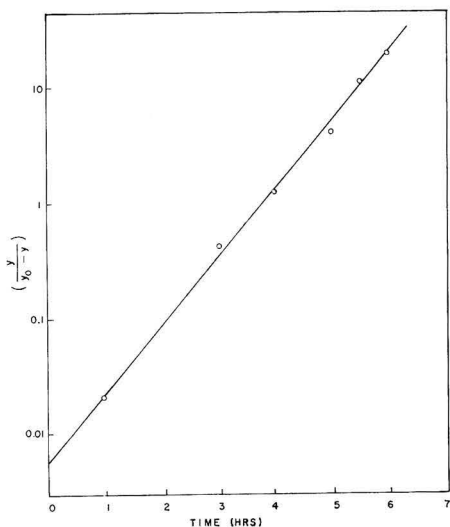Gas flow, 21.6 s.c.f.m.; inlet SO_2, 1.45%; solids rate, 39.6 lb./hr.

Figure 4. Semilog plot of fixed bed data

eral hundred pounds of alkalized alumina were charged into the shaft-filter-sorber. The unit was then operated with zero flow of solids (*i.e.*, as a horizontal-flow packed bed, to determine the sorption rate and capacity of the material). Under the following conditions: temperature, 400° F.; inlet gas flow, 21.6 s.c.f.m.; and inlet SO_2 mole fraction, 0.0133. The percentage of SO_2 removal decreased to zero in about 6 hr. Figure 2 shows the time behavior of the SO_2 removal capacity during this period.

Six hours after the start of the experiment, when the SO_2 sorption rate had decreased essentially to zero, the natural frequency vibrating feeder was turned on and a solids flow rate of 53 lb./hr. was established. Under these conditions, a steady-state operation was obtained in less than 2 hr., with a 99% SO_2 removal efficiency. The time behavior during this period is indicated by the experimental points plotted in Figure 2. Figure 3 shows similar results for a run with a solids flow rate of 39.6 lb./hr.

The time behavior during a fixed-bed period has been reported (Baasel and Stevens, 1961; Lempel in Bienstock, Field, *et al.*, 1967). Let the coordinate x represent distance into the bed and Θ the time from the start of the experiment. If we assume that the rate of sorption may be represented as proportional to the product of the concentration by weight of SO_2 in the gas with the unreacted fraction of solid, the gas phase material balance becomes:

$$\frac{\partial y}{\partial x} = -\frac{\rho_s}{G_g} Ky \left(1 - \frac{\mu}{\mu_0}\right) \tag{1}$$

The sorbent-phase material balance is expressed:

$$\frac{\partial \mu}{\partial \Theta} = Ky \left(1 - \frac{\mu}{\mu_0}\right) \tag{2}$$

Equations 1 and 2 are based on chemical reaction as rate-limiting over the full course of solid conversion. The boundary conditions are:

$$y(0,\Theta) = y_0 \qquad \mu(x,0) = 0 \tag{3}$$

where y_0 is the inlet gas concentration.

Equations 1, 2, and 3 are in a form for which a solution has been presented (Baasel and Stevens, 1961). The solution is:

$$\frac{y(x,\Theta)}{y_0} = \frac{e^{A\Theta}}{e^{A\Theta} + e^{Bx} - 1} \tag{4}$$

where

$$A = \frac{Ky_0}{\mu_0} \quad \text{and} \quad B = \frac{K\rho_s}{G_g}$$

To verify that Equation 4 does give a valid representation of the fixed-bed run, it may be noted that it predicts that a plot of $\ln[y/(y_0 - y)]$ vs. Θ, for a given bed thickness, l, should be linear, with slope A and vertical intercept $-\ln(e^{Bl} - 1)$. Figure 4 is such a plot and is seen to be linear. From the slope and intercept, the values $Bl = 5.13$ and $A = 1.35$ hr.$^{-1}$ are obtained. With the given conditions, this represents a K value of 12 hr.$^{-1}$ and a sorption capacity of 26 g. SO_2 per 100 g. alkalized alumina. The K value is below the value 29 hr.$^{-1}$ reported by the Bureau of Mines for their fixed-bed work at 626° F. This discrepancy may be due to the condition of the material used. However, it is representative of the data, as seen by Figure 4, and may be used to predict the moving bed behavior.

During a steady period of moving bed operation, it has been

shown that Equation 2 must be replaced by the following (Zahradnik, Toor, et al., 1968, Bueno, 1968):

$$\frac{G_s}{\rho_s} \frac{\partial \mu}{\partial z} = Ky \left(1 - \frac{\mu}{\mu_0}\right) \tag{5}$$

where the coordinate z is the height of the bed, measured downward from the top of the cross-flow section. If a new variable, t, is defined $t = z\rho_s/G_s$, then Equation 5 transforms to Equation 2 with t replacing Θ. Again, Equation 4 gives the SO_2 concentration at any t and x.

The concentration of interest, however, is the average outlet concentration, $\bar{y}$, which may be obtained by definition

$$\bar{y} = \frac{1}{\tau} \int_0^\tau y(l,t) \, dt \qquad \tau = \frac{h\rho_s}{G_s} \tag{6}$$

This average assumes uniform gas flow through the bed. If the substitution of Equation 4 into Equation 6 and the indicated integration are carried out, the average outlet concentration becomes:

$$\frac{\bar{y}}{y_0} = \frac{1}{A\tau} \left[\ln \left(e^{A\tau} + e^{Bl} - 1\right) - Bl\right] \tag{7}$$

Equation 7 may be used to predict the SO_2 removal efficiency under steady-state operating conditions. During a transient period, however, such as that encountered between the sixth and eighth hours of the experimental run shown in Figure 2, neither Equation 4 nor 7 represents the outlet composition. Since during this time, sorbent loading is changing both as a function of time, Θ, and position, t, the material balance equation must be written as follows:

$$\frac{\partial \mu}{\partial \Theta} + \frac{\partial \mu}{\partial t} = Ky \left(1 - \frac{\mu}{\mu_0}\right) \tag{8}$$

Fortunately, a change of variables can convert this equation into a form similar to that already encountered. Define a new variable, η, by the equation $\eta = \Theta - t$ (η is merely a translation of the time axis by an amount t). This reduces Equation 8 to:

$$\frac{\partial \mu}{\partial t} = Ky \left(1 - \frac{\mu}{\mu_0}\right) \tag{9}$$

Suppose now the bed is started from a $\mu = 0$ value (this is boundary condition 4 and corresponds to the experimental condition at the sixth hour). Equation 9 is valid only for $\eta \geq 0$—i.e., for $\theta \geq t$. This simply states that Equation 9 applies only for experimental times longer than the transit time it takes for the new sorbent to make its way to a point of interest in the bed. For shorter times, no sorption can occur.

Thus Equations 1 and 9 still have as their solution Equation 4 with Θ replaced by t. However, $\bar{y}(\Theta)$, the average outlet concentration, is now given by the equation:

$$\frac{y}{y_0} = \frac{1}{\tau} \left[\int_0^\Theta y(t,l)dt + \int_\Theta^\tau 1 \, dt\right]$$

which has as its solution:

$$\frac{y}{y_0} = \frac{1}{A\tau} \left[\ln \left(e^{A\Theta} + e^{Bl} - 1\right) - Bl\right] + (1 - \Theta/\tau) \quad 0 \leq \Theta \leq \tau \tag{10}$$

A plot of Equation 8 for the experiment is included in Figure 2 using the value 1.1 hr. for τ, corresponding to a solids flow rate of 53 lb./hr. For a major portion of the transient period and for the ultimate steady-state removal, Equation 10

gives a good fit to the data. The failure of the data to follow the "corner" at 7.1 hr. is due to the idealized model used for the solids flow distribution and illustrates nature's reluctance to conform to "step change" assumptions. Similar behavior is seen in Figure 3 for the run at reduced solids flow rate. Nonetheless, the overall fit is good and indicates that the behavior of moving-bed sorbers can be predicted from static-bed models. Their combined performance as sorbers and filters is discussed in the next section.

Simultaneous Fly Ash and SO₂ Removal

Experiments have been carried out in which both SO_2 and fly ash were added to the inlet stream to the shaft-filter-sorber. The fly ash was screened to -325 mesh and was added by the described screw feeder assembly. Fly ash loadings about 2 to 3 grains per standard ft.³ were achieved with this unit.

Table I summarizes the best results obtained to date—best in the sense that the experiments ran smoothly and uniformly for the durations indicated. Table II presents the size distribution of the fly ash used as determined by sedimentation pipet.

The per cent of SO_2 removal was determined in the usual way with use of iodometric titration. The filtration efficiency reported is an overall figure, obtained by passing the entire outlet stream through a 1-μ Cuno filter. The Cuno filter cartridge was weighed before and after the experiments and the weight gain was assumed to represent the amount of solid fly ash not collected by the shaft-filter-sorber.

The pressure drop across the filter measured in both runs was 2.0 in. H_2O, and it remained constant throughout the experiment. A pressure drop of 1.5 in. H_2O was predicted

Table I. Summary of Simultaneous Removal Runs[a]

Expl. parameter	Run 6	Run 7
Gas flow rate, s.c.f.m.	31.0	31.2
Nominal space velocity, hr.⁻¹	3500.0	3500.0
Sorbent rate, lb./hr.	10.5	19.6
Temperature, ° F.	400.0	400.0
Inlet SO_2 mole fraction	0.006	0.006
Outlet sorbent loading, g./100 g.	19.0	10.0
Fly ash loading grains per ft.³	2.82	3.1
Duration of experiment, hr.	3.5	4.0
Filtration efficiency	99.3	98.7
SO_2 removal, %	100.0	100.0
Pressure drop in H_2O		
Calculated	1.5	1.51
Observed	2.0	2.0

[a] Sorbent was 1/16-in. alkalized alumina beads.

Table II. Size Distribution of Fly Ash Used

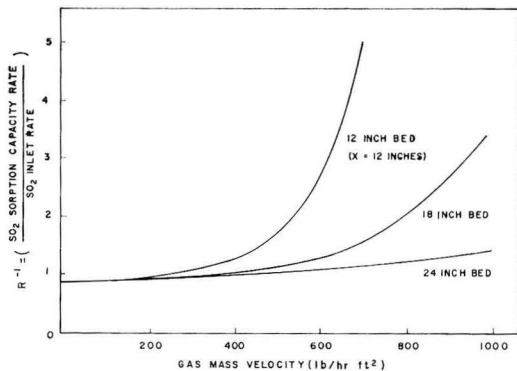| Particle radius, μ	% Less than
52.4	100.0
41.6	75.5
35.8	50.0
30.4	40.0
27.0	23.6
19.8	17.0
16.0	13.9
13.7	11.0

Figure 5. Effect of gas mass velocity and bed thickness on required sorption capacity rate (90% removal)

by use of the Ergun equation to estimate the bed friction factor. Thus, the presence of the fly ash, under the stated conditions, has only a slight effect on the overall pressure drop across the unit.

With the rate and capacitance parameters evaluated earlier, Equation 7 predicted a 99+% SO_2 removal efficiency, in agreement with the observed results.

The high filtration efficiency indicates that sorbent-pebble filters can be used to remove fly ash while simultaneously removing gaseous SO_2.

Discussion

Results described in this paper have shown that the shaft-filter-sorber can be successfully implemented to remove SO_2 and fly ash from gas streams. Moreover, the behavior of such units may be predicted if suitable sorption rate models are available.

The predictive Equation 7, derived for the rate equation given as the r.h.s. of Equation 1, describes adequately the SO_2 removal in all the runs made thus far on the experimental unit. This rate expression has been doubted, and other reaction models postulating alternate controlling steps have been proposed (Equation 5). However, these expressions offer no immediate advantage over the one used in this paper, although if other rate expressions are found to describe the sorption process better, the techniques developed here may be used to derive a relationship similar to Equation 7 for the improved rate expression (Schoenberg, private communication).

The results reported in Table I show that complete gas cleaning is technically possible with use of a shaft-filter-sorber. However, if this unit is used commercially, higher gas flow rates and lower sorbent flow rates are required. To give some idea of the relationship between these quantities, a quantity R is defined as:

$$R = \frac{A\tau}{Bl}$$

R represents the inlet flow of SO_2 divided by the inlet flow of SO_2 sorption capacity:

$$R = \frac{\text{inlet flow of } SO_2}{\text{inlet flow of } SO_2 \text{ sorption capacity}}$$

Thus $1/R - 1$ represents the excess amount of sorbent above the stoichiometric amount required to achieve a given per cent

SO_2 removal. In terms of R, Equation 7 is rewritten:

$$\frac{y}{y_0} = \frac{1}{BlR} [\ln (e^{BlR} + e^{Bl} - 1) - Bl] \quad (11)$$

Figure 5 presents a plot of this equation in which the reciprocal R value required to achieve 90% SO_2 removal is plotted *vs.* the gas mass velocity, for three bed thicknesses. From an overall design viewpoint, operation will probably be carried out on that portion of the curves beyond which small increases in gas mass velocity require large increases in R^{-1}. Finally, it should be noted that Equation 11 provides a means for determining the effect of individual design variables on shaft-filter-sorber performance. For example, the effect of bed height, h, on performance could be predicted from Equation 11 in terms of its relationship to R.

The experimental points represented in Table I correspond to gas mass velocities of 150 lb./hr. ft.[2] and reciprocal R values of 1.38 and 3.44. From Figure 5 it is seen that these sorbent rates are in excess of those required to achieve 90% SO_2 removal. In fact, the sorbent rate could be lowered to 7 lb./hr. and the unit should still achieve 90% SO_2 removal. Conversely, at the higher sorbent feed rate, the unit could accept a gas mass velocity of 600 lb./hr.ft.[2] and still maintain 90% SO_2 removal. These figures better represent the commercial feasibility of such a unit and provide targets for future experiments. At higher flow rates, the pressure drop would, of course, be higher than the 2 in. of water observed in the present experiments. However, this effect can be computed from the standard correlations for packed beds (Ergun, 1952), and this factor would have to be considered in determining optimum operating conditions.

Another factor to be considered in the operation of units such as a shaft-filter-sorber is the attrition loss of the solid sorbent material. No information was generated on attrition loss in the experiments performed; it is reasonable to conjecture that such loss would be less than that encountered in units where solids contact is more violent, *e.g.*, entrained or fluidized beds.

Acknowledgment

Nomenclature

A	= parameter grouping, Equation 5
B	= parameter grouping, Equation 5
G_g, G_s	= mass velocities of gas and sorbent, lb./hr. ft.[2]
h	= height of active portion of sorbent bed, ft.
K	= reaction rate constant, hr.[-1]
l	= bed thickness, ft.
R	= ratio of SO_2 inlet rate to SO_2 removal capacity
t	= alternate coordinate, hr.
x	= distance coordinate into bed, ft.
y	= SO_2 concentration in gas, by weight
z	= distance coordinate relating to bed height, ft.
η	= translated time scale
Θ	= time, hr.
μ	= SO_2 concentration on absorbent, by weight
ρ_s	= solids bulk density, 58 lb./ft.[3]
τ	= value of t at $z = h$

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Isoprene: Identified as a Forest-Type Emission to the Atmosphere

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■ The hemiterpene isoprene (2-methyl-1,3-butadiene) until recently has not been considered to be present in natural plant products. Direct gas chromatographic, infrared, and mass spectrometric analyses of the air in contact with the plant foliage for five common tree species confirm previous observations (Rasmussen, 1964) of the existence of isoprene as a plant product. Preliminary data from surveying the dominant forest tree species of North America indicate that the frequency of occurrence of isoprene is similar to that of α-pinene although species differ. Isoprene has been resolved directly from the out-of-doors air over mango foliages in Panama at concentrations of 0.5 to 24 p.p.b. in 5 ml. of air. The biological and air chemistry fates of isoprene are discussed.

T here exists an extensive literature describing the composition of essential oils and leaf oils for numerous plant species (Guenther, 1949; Pridham, 1967; Simonsen, 1953). In none of this literature is isoprene (2-methyl-1,3-butadiene) described as a major component of plant products. Many investigators have concluded from both their own studies and literature surveys (Fisher, 1954; Sandermann, 1962; Weissmann, 1966) that isoprene itself is apparently not present in natural products. Bonner (1950) in his classic textbook of plant biochemistry states that isoprene is not a natural plant product.

Recently, the occurrence of isoprene in plant material has been reported by several investigators. Rhoades (1960) and Radtke, Springer, *et al.* (1963) identified isoprene as a volatile component of roasted coffee. Gil-Av and Shabatai (1963) reported isoprene to constitute 50–80% of the total unsaturated gaseous hydrocarbon in tobacco smoke. However, isoprene was not isolated from the tobacco leaf itself.

The volatile hop oil constituents have been extensively studied by Buttery, McFadden, *et al.* (1963, 1964) and isoprene was identified by capillary gas chromatography retention times, infrared structure, and mass spectra. The relative percentages of isoprene in five European hop steam distillates ranged between 0.06–0.1%. It has not been definitely estab-

lished that isoprene is present in the hops on the vine. However, Hartley and Fawcett (1967) showed hops contain reasonably large quantities of 2-methylbut-3-en-2-ol which could readily dehydrate to isoprene in the drying of the hops, in the steam distillation of the oil, or in the gas chromatography apparatus.

Rasmussen (1964) and Rasmussen and Went (1965) observed a hemiterpene tentatively identified as isoprene emanating from oak leaves, aspen, and sweetgum foliages during *in situ* studies using a gas chromatograph in remote natural areas in the United States. The identification was based on relative retention time data by use of dissimilar substrates. Previously Sanadze and Dolidze (1961) in Russia had found peaks in the molecular weight regions corresponding to isoprene, butane, and propane in mass spectrometric analyses of the freeze out condensates of the air in contact with the foliages of *Amorpha fructicosa* (L.), the false indigo; *Buxus* (sp.), boxwood; and *Quercus iberica* (Bieb.), the iberian oak.

This current paper presents evidence that it is indeed isoprene which is involved in these leaf emissions. A thorough proof of structure is presented based on direct gas chromatographic, infrared, and mass spectrometric analyses. Also this paper presents evidence that the emission of isoprene occurs under natural conditions from the intact, living foliage of numerous plant species.

Experimental

Apparatus. The gas chromatographic equipment used in the study was a Hewlett-Packard Model 5751-B, a Perkin Elmer Model F11, and a Beckman GC-5 with flame ionization detectors. All columns were constructed of 0.125-in.-o.d., 0.105-in.-i.d., 304 stainless steel tubing. For readout a 1 mV potentiometric recorder was used with chart speed of 30 in. per hour.

Column A was 6 ft. in length, packed with 4% Carbowax 20M on HMDS-treated Chromosorb W, acid wash, 60- to 80-mesh. Column temperature was maintained at 60° C., injector temperature was 170° C., detector temperature was 250° C. Helium flow rate was 50 ml. per min. Sample sizes varied between 1 and 5 ml. All samples were prepressurized to inlet pressure before injection using Pressure-Lok gas syringes (Precision Sampling Corp.).
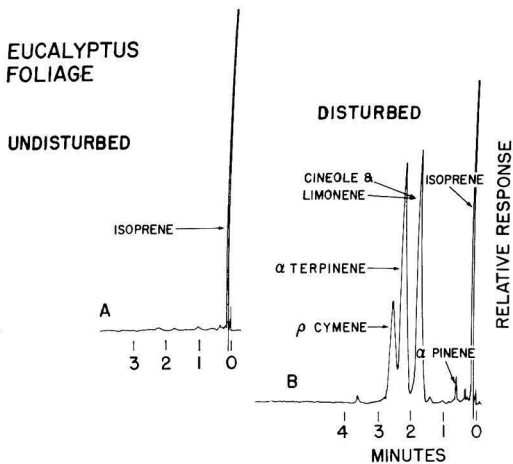
Figure 1. Chromatograms of the volatile organic material from *Eucalyptus camaldulensis* **leaves**

A. Undisturbed foliage
B. Same foliage disturbed by handling when placed in study chamber

Column B was 7 ft. in length and packed with Porapak Q, 100- to 120-mesh. Column temperature was 150° C., injector temperature was 180° C., and detector temperature was 250° C. Helium flow rate was 45 ml. per min. Sample size was varied between 1 and 5 ml.

Column C, 6 ft. in length, packed with Porapak Q, 100- to 120-mesh, was used only in the Beckman GC-5. Column temperature was programmed: 25° C. was maintained for the first 1.5 min. during injection disturbance and the air–methane peak elution; at 1.5 min. the temperature was jumped to 70° C.; at 2.0 min. the program was begun at a rate of 12.5° C. per min.; and at 180° C. the temperature was held for 10 min. Helium flow rate was 30 ml. per min.

Infrared spectra were obtained using a Perkin Elmer Model 221 spectrophotometer (NaCl optics) with a 10-m. path length cell.

Mass spectra were determined using an Associated Electronics Industries, Model MS-12 mass spectrometer.

Materials

The foliages studied were on intact plants in leaf assimilation chambers (volume 2 liters) under static conditions. The light intensity was 1100 ft. candella and the temperature was 28° C. The light quality was a mixture of Gro-Lux and cool white fluorescent tubes and incandescent bulbs. The relative humidity reached 92%+ r.h. in the closed chamber within 10 min. Foliages of 300 to 500 cm.^{2} total area were kept in the chambers for varied lengths of time, usually 2 hr.

The increasing concentration of the foliage-released volatile organic (isoprene) was monitored using 1-ml. gas samples injected into the gas chromatograph and peak height measured. Either column A or B was used to quantitate the peak height of the foliage volatile (isoprene) by converting peak height to concentration in parts per million (p.p.m.). An analyzed gas mixture (Scott Research Laboratories) of 8.3 p.p.m. of isoprene by volume in nitrogen was used as a reference concentration.

When the concentration of isoprene in the chamber reached 15 to 20 p.p.m., 1 liter of air in the chamber was transferred by a syringe pump to a saran (type 18-100) plastic gas sampling

bag (volume 5.5 liters). The transfer procedure was repeated until a concentration of 10 p.p.m. was measured in the gas sampling bag; usually 4 liters were transferred. The saran bags did not contribute any measureable volatiles to the stored samples, and no appreciable wall adsorption was observed even after three days. The accumulated foliage volatiles in the gas sampling bags were usually analyzed by infrared and mass spectroscopy within four hr. after collection.

The species whose foliage volatiles were studied by infrared and mass spectrometry were: red oak, *Quercus rubra* (L.); eastern cottonwood, *Populus deltoides* (Bartr.); sweetgum, *Liquidambar styraciflua* (L.); white spruce, *Picea glauca* [(Moench) Voss.]; and the Australian river red gum, *Eucalyptus camaldulensis* (Dehn).

Results and Discussion

The presence of isoprene as indicated by gas chromatographic (gc) retention time data was observed in more than 30% of the 230 plant species surveyed. (A complete list of the species studied will be published separately.) The gc profiles for these many different kinds of plants studied indicated a variety of genetic and physiological factors involved in the release of the foliage volatiles resolved. The following selected analyses are described.

Broadleaf Foliages. Figure 1A is a chromatogram of 1 ml. of the air in contact with undisturbed eucalyptus leaves. The only component resolved is isoprene.

When the foliage was disturbed either by handling or blowing in a wind, subepidermal schizo-lysigneous oil glands were ruptured releasing a variety of monoterpenes. Figure 1B shows the chromatogram of the air in contact with the disturbed foliage. The same phenomenon for undisturbed *vs.* disturbed foliage was observed for sweetgum foliage.

The nonaromatic foliages of oaks, willows, aspens, cottonwoods, and plane-trees released only isoprene in any ap-
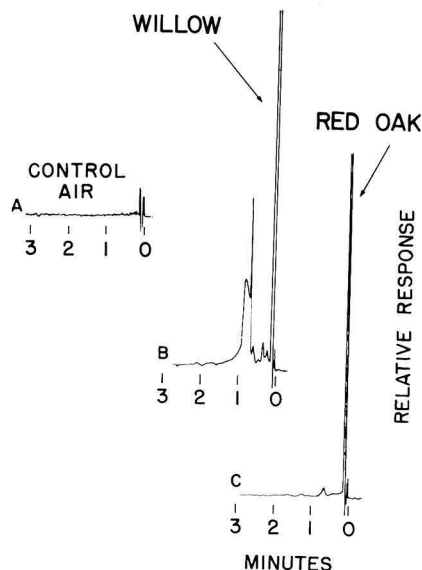
Figure 2. Chromatograms of the leaf volatiles from nonessential oil foliages. Compounds through C$_4$ missed in the negative disturbance caused by the oxygen in the air sample

A. Control air in chamber
B. *Salix babylonica*
C. *Quercus rubra*

Table I. Comparison of GC and Infrared Data for Foliage Volatile with Isoprene

| | Concn. p.p.m. | Retention times min.[a] | | Absorption peaks wave no. (cm.$^{-1}$) | |
		Unknown	Isoprene	Unknown	Isoprene
Oak	12	10.2	10.2	990, 908, 895	990, 908, 895
Cottonwood	8	10.2	10.2	990, 908, 895	990, 908, 895
Sweetgum	6	10.2	10.2	988, 910, 897	990, 908, 895
Eucalyptus	5	10.3	10.3	[b] 908, 895	990, 908, 895
White spruce	4	10.2	10.2	[b] 910, 897	990, 908, 895

[a] Conditions column B program.
[b] Concentration too low to resolve the 990 cm.$^{-1}$ peak.

preciable quantity. Figure 2A shows an insignificant level of organics in the control air. Figures 2B and 2C represent the chromatograms for willow and oak leaf emanations, respectively. The chromatogram of the willow foliage volatiles shows leaf alcohols and other unknown components due to excessive transpiration sustained by the willow foliage enclosed for 4 hr. This is a common observation for foliages enclosed for more than 3 hr. The gas chromatographic analysis of the oak foliage volatiles shows an almost 100% purity of isoprene in Figure 2C.

Some of the observations from smelling these accumulated foliage volatiles at concentrations of a few p.p.m. are of note. The eucalyptus and the sweetgum terpenoid odors were very strong for the disturbed foliages. However, the odors of the undisturbed foliages had the distinctive hydrocarbon odor of isoprene, against the background of the respective eucalyptus or sweetgum odor. The odor of isoprene was very characteristic of the nonaromatic foliages like oak, willow, aspen, palm, fig, and plane-tree leaves. It is especially interesting to note that when a group of 16 people in the laboratory was asked to smell these accumulated foliage isoprene volatiles from the nonaromatic leaves, the description given most often was "smells like an oak forest." The response for smelling nonisoprene releasing foliages like maples, ash, birches, and alders was "smells like fresh leaves."

The volatile compound from oak leaves, trans-2-hexenal, which Riddiford (1967) found stimulated female polyphemus moths to release their sex pheromones, was not detected in the gaseous organics of accumulated oak foliage volatiles. The retention times of trans-2-hexenal and isoprene at 200° C., on the Porapak Q column (B) were 28.6 and 4.2 min., respectively. The lower detection limits for gaseous trans-2-hexenal were 35 p.p.b. in 5-ml. air samples. For the various oaks studied—red, white, black, and pin oak—foliage isoprene would accumulate to concentrations between 10 to 40 p.p.m., whereas trans-2-hexenal or hexenal was never observed.

The method used by Riddiford for isolating trans-2-hexenal was vacuum distillation of freshly ground oak leaves which produced a distillate collected in a bath of dry ice and acetone. Subsequent preparative gas chromatography, bioassay, infrared and mass spectral analyses demonstrated that the isolated active component was trans-2-hexenal.

Although trans-2-hexenal is ubiquitous in green leaves, it is not appreciably emitted by undamaged leaves. Yet, it is associated with many varied responses in insect communications and a specific mating response in polyphemus moths. Obviously, volatile leaf factors should be studied more rigorously for comparing both leaf extracts and normal foliage emanations.

Conifer Foliages. Analysis of the air in contact with conifer foliages, i.e., pines, firs, hemlocks, junipers, and spruces,

showed that only the genus Picea (spruce) released isoprene as a foliage volatile. Conifer foliages release a variety of monoterpenes which in certain species are characteristic of the species. Isoprene was observed to emanate from white, P. glauca [(Moench) Voss.]; red, P. rubens (Sarg.); black, P. mariana [(Mill.) B.S.P.]; and blue spruce, P. pungens (Engl.) tree needles but not from the needles of the Norway spruce. The emanation of terpenes from spruce needles was greatly diminished when transpiration was diminished. The emanation of isoprene from the spruce needles did not respond to short-term fluctuations in transpiration.

The observation of isoprene emanating from eucalyptus and spruce foliages is especially interesting as isoprene has never been reported to be a constituent of their leaf oils. Both genera, Eucalyptus (Penfold and Willis, 1961) and Picea (von Rudloff, 1964, 1966a,b), have been extensively studied. A possible interpretation is that isoprene does not accumulate to an appreciable level in the foliage tissues and therefore is not measured as a constituent in the leaf oil extracts. An alternate interpretation is that very small amounts are present in the leaf tissue but are lost in the handling procedures of making leaf oil extracts. Data from physiological studies (Rasmussen, 1969) suggest that the isoprene that is synthesized is rapidly volatilized to the atmosphere.

Identification of Isoprene. Direct infrared and mass spectroscopy analyses of the air in contact with plant foliages were made to avoid possible structural changes in the compound due to thermal handling techniques or possible artifact contamination. Direct analyses were possible because, in the foliages studied, isoprene was the major component being released (90%+ purity) and the concentration of 10 p.p.m. in air was within the lower sensitivity limits of the infrared and mass spectroscopy instrumentation used.

Table I shows the pertinent gas chromatographic and infrared data for the foliage volatiles of five different tree species compared with the known isoprene standard. The agreement for both the gas chromatography and infrared data is very good between the foliage volatile and the isoprene standard.

Cochromatographing isoprene with the foliage volatile gave a single peak with no shoulders. Porapak Q was the column support of choice for exact retention time data, resolving isoprene from pentene, pentane, isopentane, cyclopentene, cis- and trans-2-pentene, and cis- and trans-2-butene adequately enough for relative retention time identification.

Isoprene's retention time of 10.2 min. at 150° C., on Porapak Q (B) was too long to monitor the changing concentration of isoprene under the physiological conditions used. For these needs the Carbowax 20M, 4% 6-ft. column was found to be better suited with a retention time for isoprene of 0.20 min. The Carbowax 20M column program (A) was used to monitor and quantitate the concentration of isoprene for transfer to the

Table II. Comparison of $m./e.$ Percentages for Isoprene and Foliage Volatiles[a]

$m./e.$	Isoprene	Oak	Cottonwood	Sweetgum	White spruce	Eucalyptus
68	100.0	100.0	100.0	100.0	100.0	100.0
67	113.63	115.3	114.4	116.6	116.7	117.4
53	154.54	146.8	140.7	125.0	127.3	125.4
39	163.63	165.4	166.2	170.0	169.5	167.7

[a] Conditions: Room inlet, 24° C.; source inlet, 150° C.; acceleration voltage, 8 kV; electron energy 78 eV; trap current, 100 microamps; magnetic scan on MS-12.

PARENT ION
m/e 68

BASE ION
m/e 67

$$H\overset{|}{\underset{|}{\text{--}}}CH_2$$
$$C\text{--}CH=CH_2 \longrightarrow C_3H_3 + RESIDUE$$
$$CH_2 \quad m/e\ 53 \qquad m/e\ 39$$
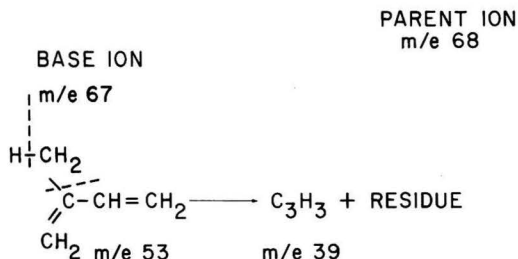
Figure 3. Fragmentation scheme for isoprene

MANGO
FOLIAGE

SHELTERED

ISOPRENE

B

AIR

n-BUTANE

A

OPEN

RELATIVE RESPONSE

8   6   4   2   0
MINUTES
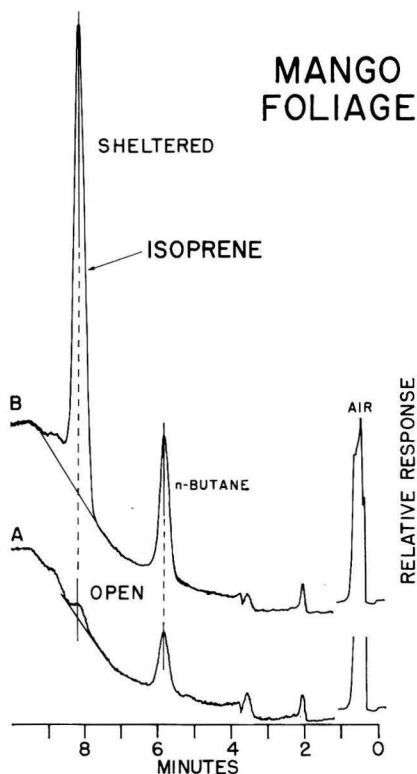
Figure 4. Programmed temperature gas chromatographic analysis of the organic volatiles in the air next to *Mangifera indica* foliage under field conditions

A. Open-unsheltered foliage
B. Same foliage, sheltered

gas sampling bags and subsequent infrared and mass spectra analyses.

From the gas sampling bag, the foliage volatiles (90%+ isoprene) were bled into the evacuated 10-m. cell. Infrared spectra were obtained on concentrations between 4 to 12 p.p.m. The 3.6-liter volume of the 10-m. cell was at atmospheric pressure after transfer of the foliage volatiles from the saran bag.

Absorption maxima at 990, 908, and 895 cm.$^{-1}$ (Table I) were characteristic of isoprene at 10 p.p.m. in air and were used in the identification of the foliage volatiles. Unfortunately, the 1600 to 1650 cm.$^{-1}$ bands indicative of stretching vibrations of conjugated olefin structure were obscured by the intense water absorption between 1900 to 1300 cm.$^{-1}$ The two strongest bands near 900 cm.$^{-1}$ were intense enough to enable isoprene to be identified at 4 p.p.m. The doublet peaks near 900 cm.$^{-1}$ indicate vinyl or terminal olefin structure.

The mass spectra of isoprene and the foliage volatile were identical with a parent ion having a mass to charge ratio ($m./e.$) of 68, representing the molecular weight of isoprene and a base peak of $m./e.$ 67 formed by the loss of a single H atom. The other prominent peaks were $m./e.$ of 53 from the loss of a methyl group and $m./e.$ of 39 which is the possible cyclopropene ring from skeletal rearrangement. Figure 3 shows the fragmentation scheme for isoprene.

Table II gives the percentages of the abundant ions ($m./e.$) ratioed against the intensity of the parent peak, $m./e.$ of 68. The agreement is very good for the oak and cottonwood foliages with the isoprene standard spectra. These isoprene foliage volatiles were almost pure isoprene: 99%. The spectra for the sweetgum, white spruce, and eucalyptus foliages which were all contaminated with small amounts of monoterpenes from the aromatic foliage had less neatly matching spectra. However, their mass to charge spectra are similar to that of the isoprene standard.

The identification of the foliage volatile from five tree species by mass spectra and infrared structure further validates the relative retention time data indicating that the peak so often observed to be the major component in the foliage volatiles for many broadleaf tree species is isoprene. At present isoprene has been measured in the foliage volatiles of 35 plant genera. Direct analysis has avoided the possibility that the component identified as isoprene was the result of thermal or dehydration effects due to collection or isolation procedures.

In Situ Foliage Studies. Figure 4A shows isoprene resolved directly from the air over mango [(*Mangifera indica*, L.)] leaves, out-of-doors at the Miraflores Laboratory in the Canal Zone, maintained by the U.S. Army Tropic Test Center. The peak size represents a concentration of 0.6 p.p.b. in a 5-ml. sample. The analysis of the same branch of foliage sheltered by a paper cone to minimize wind movement over the foliage but not to shade or totally enclose the leaves from gaseous exchange with the atmosphere is shown in Figure 4B.

Table III. Composition of North American Forest Regions/Foliage Terpenes

Region	No. major trees species	No. α-pinene	No. iso-prene	% Terpene emitters
Northern	20	8	6	70
Central hardwood	16	3	5	50
Southeastern	18	4	4	44
Rocky Mt.	13	10	4	100+
Pacific Coast	24	15	7	92

The sample was taken 45 min. after the leaves were sheltered. The increase in the isoprene peak was 40-fold, representing a concentration of 24 p.p.b. in a 5-ml. sample. Thus, it is apparent that the leaves of the mango tree were continuously releasing into the atmosphere trace concentrations of isoprene. This emanation of isoprene was observed only when the leaves were in the presence of sunlight. No isoprene was measured to be released during the night.

Isoprene was also observed at the Miraflores Laboratory from the foliages of coconut palm, Cocos nucifera (L.); Panama hat palm, Carludovica insignis (Duch.); bamboo, Bambusa (sp.); higo fig, Ficus costaricana [(Liebn.) Mig.]; and a legume tree, Inga spectabilis [(Vahl) Willd].

From the present preliminary survey of the dominant forest tree species of North America, the occurrence of foliage isoprene in vascular plants is common. Its frequency of occurrence is almost as great as that of α-pinene as a foliage emanation. Table III relates the composition of the five North American forest regions with the type of foliage emission. The data indicate that the emission of the monoterpene, α-pinene, and the hemiterpene, isoprene, is a widespread phenomenon.

The fate of these two reactive materials in the atmosphere is possibly similar to the fate of the olefins from automobile exhaust. In the Haagen-Smit (1952) photochemical mechanism for smog formation, olefins, nitric oxides, and sunlight react to form ozone, peroxyacylnitrate-like compounds and aerosol material. Went (1960, 1966) proposed a similar fate for the terpene emissions in the atmosphere. The aerosols produced (Aitken nuclei) are believed to be responsible for the natural atmospheric blue haze associated with vegetation.

The biological fate or interactions of foliage emissions is at present very poorly understood. In the laboratory Rasmussen, Hutton, et al. (1968) observed that the organic volatiles emanating from tropical foliages can be utilized by wild populations of fungi as the sole carbon source for growth. Furthermore, the data suggested that the naturally occurring organic volatiles beneath the canopy of the tropical forest are produced as well as utilized by the microbial life growing epiphytically on the vegetation surfaces. These studies suggested that naturally occurring organic volatiles are disposed of in a biological sink.

Presently, further studies are being pursued to define more precisely the biological and air chemistry fate of the ubiquitous terpenoid emissions of plant foliages.

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Automatic Sequential Sampling of Atmospheric H₂S by Chemisorption on Mercuric Chloride-Treated Paper Tape

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■ Concentrations of atmospheric hydrogen sulfide from 0.5 to 100 parts per billion may be conveniently monitored by use of an automatic, sequential, filter paper tape sampler and mercuric chloride-treated paper tape. This method is especially suited to field sampling because no liquid reagents are employed, the samples obtained are stable over long periods of time, and a single roll of tape is sufficient for collecting consecutive 2-hr. samples over a period of 1 month. The disadvantages of the lead acetate tape method have been overcome by modification in sampler design and by use of mercuric chloride reagent.

T he lead acetate tape method for continuous sequential sampling of hydrogen sulfide in concentrations of from 0 to 100 parts per billion (Sensenbaugh and Hemeon, 1954) has been commonly used to measure hydrogen sulfide air pollution because of its convenience, low cost, and simplicity. It has been found, however, that low results are obtained with this method because the lead sulfide formed readily reacts with air, oxidants, sulfur dioxide, and light (Bamesberger and Adams, 1969; Paré, 1966; Sanderson, et al., 1966;

Smith, et al., 1961). To take advantage of the paper tape sampling technique and to avoid the limitations posed by the lead acetate reagent, a mercuric chloride-impregnated tape method was developed by Paré (1966). This method, which involves automatic sequential sampling of atmospheric hydrogen sulfide by chemisorption on mercuric chloride-treated paper tape, was investigated and modified accordingly. Parameters investigated were the effects of humidity and reagent composition, range and sensitivity, linearity of response, stability of exposed and developed tapes, interferences, and reproducibility.

Experimental

Tape impregnated with mercuric chloride was not commercially available; therefore, an apparatus for impregnating and drying the tape was designed (Figure 1). With this device, a 100-ft. roll of Whatman No. 4 paper tape can be prepared in 30 min. The cabinet temperature was 123° F. The impregnating reagent used consists of 30 g. of mercuric chloride, 40 ml. of glycerol, and 5 g. of urea in 1 liter of 95% ethanol. (**Caution:** *mercuric chloride is highly poisonous. If spilled on skin, flush off with water immediately. Use plastic gloves in handling tapes.*)

An automatic, sequential tape sampler manufactured by

Figure 1. Tape impregnator and dryer

1. GUIDE SPOOLS
2. UP TAKE SPOOL (MOTOR DRIVEN)
3. GLASS SPOOL FOR IMPREGNATION
4. SOLUTION VAT
5. STORAGE SHELVES
6. TAPE

7. DRIVE MOTOR - 3 ft/min
8. HEATING UNIT - 500 WATTS
9. FAN - 150 cfm
10. HINGES
11. GLASS WINDOW
12. EXHAUST VENT
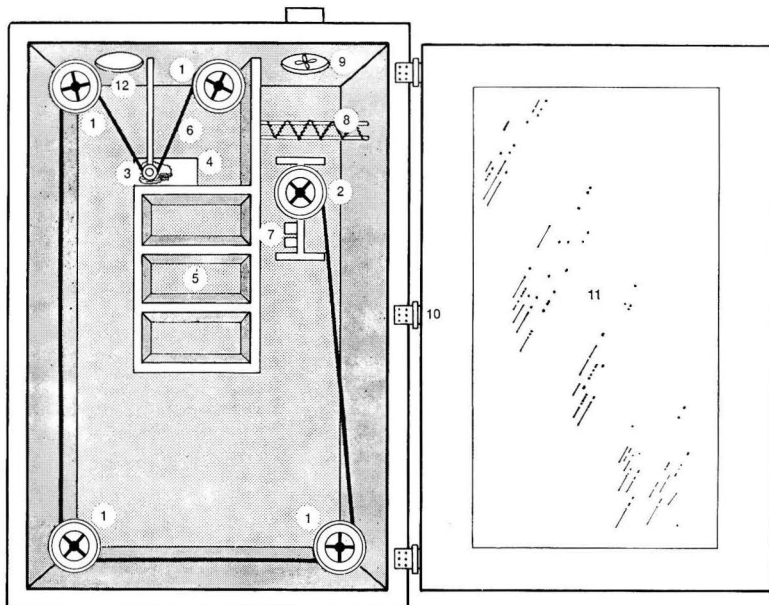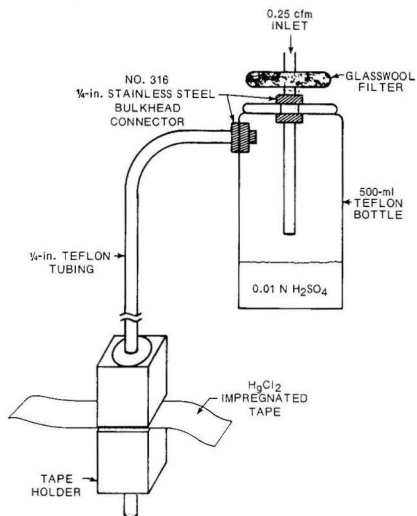
Figure 2. Tape sampler modifications

Figure 3. Apparatus for producing controlled concentrations of hydrogen sulfide in p.p.b.

the Research Appliance Co. was used for collection of air samples. It was necessary to modify the sampler intake system to prevent loss of hydrogen sulfide. Soft metal containers, fittings, and tubing used in the original construction of the humidifier and in the rest of the intake system were changed to stainless steel and Teflon and the line was shortened (Figure 2). The sample stream was filtered through Pyrex glass wool plug prior to being impinged on the surface of the 0.01N sulfuric acid contained in the humidifier bottle. The glass wool was contained in a 35-mm. disposable, clear, cellulose acetate-butyrate filter holder manufactured by

Millipore Filter Corp. With this humidifier operated at 75° F., dry air entering the device exits at approximately 50% relative humidity. Atmospheric samples were collected on the impregnated filter tape by sampling with this modified tape sampler at a flow rate of 0.25 cu. ft. per min. for 2-hr. intervals. The range of concentration measurable at this sampling condition is from 1 to 15 p.p.b. Higher concentrations can be measured by reducing the sampling rate or time. After the roll of tape was exhausted, it was removed from the instrument and placed in an airtight plastic bag for storage. The plastic bag, made of polyester with polyethylene lining, is heat sealable and was obtained from Aloe Scientific. Protect the sampler and tape from direct sunlight as there is some indication that sunlight causes tape darkening.

The exposed tape was removed from the plastic bag, loosely unwound about itself and placed on a glass shelf inside of an airtight chamber constructed of stainless steel and glass. About 300 ml. of fresh concentrated NH₄OH in a shallow dish was placed on the bottom of the chamber. The tape was

Figure 4. Response of HgCl₂ tape at different reagent compositions and relative humidities
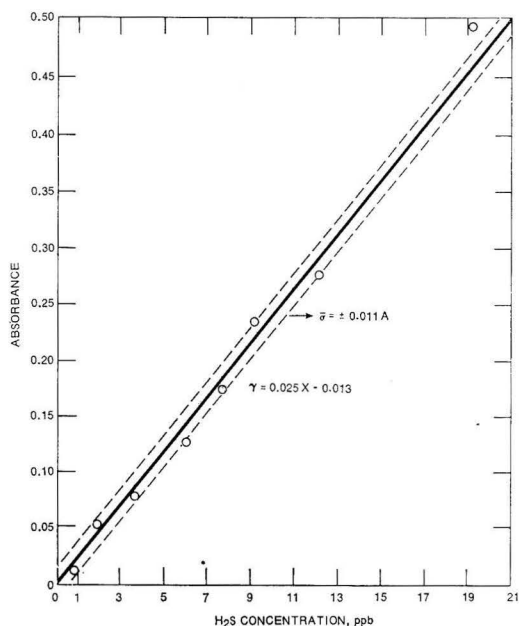
Figure 5. H₂S calibration curve (2-hr. samples at 0.25 c.f.m.)
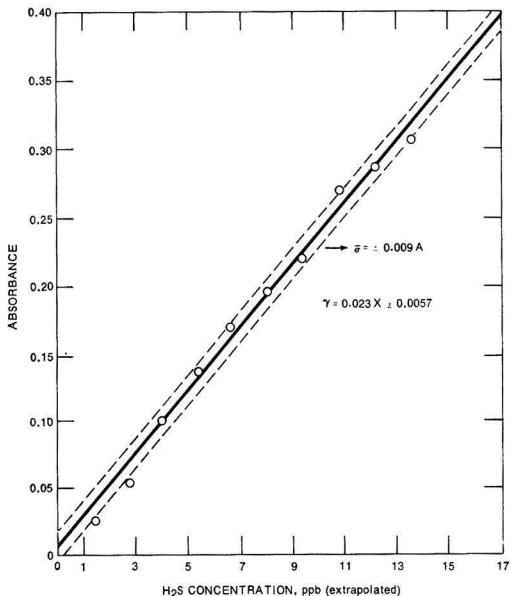
Figure 6. H₂S calibration curve (1 to 10 min. samples at 0.25 c.f.m.)

$\bar{\sigma} = \pm 0.009 \, A$

$\gamma = 0.023 \, X \pm 0.0057$

Figure 8. Stability of HgCl₂ tape prior to development

H₂S ADDED 7.0 ppb (THEORETICAL)

Figure 7. Apparatus for producing controlled high-level concentrations of hydrogen sulfide in p.p. 10 m.
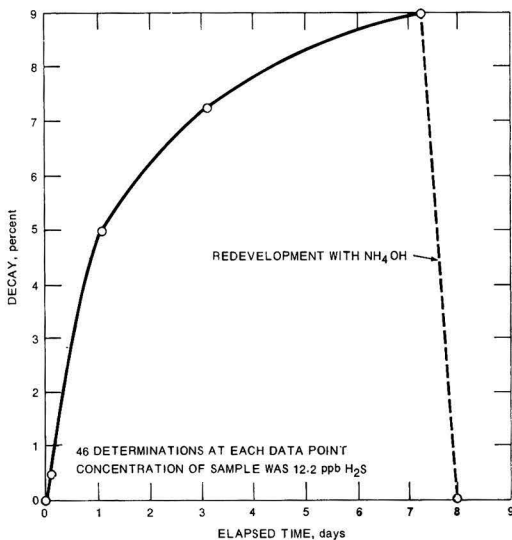
Figure 9. Decay rate of developed tapes

REDEVELOPMENT WITH NH₄OH →

46 DETERMINATIONS AT EACH DATA POINT
CONCENTRATION OF SAMPLE WAS 12.2 ppb H₂S

left in the chamber for at least 12 hr. The humidified tape was then removed and dried using the apparatus described in Figure 1 except that it was not passed through the reagent tray and the cabinet temperature was 90° F.

Absorbance of the brown stain that developed on treatment with ammonia was determined with a spot evaluator available from Research Appliance Co. Adjacent clean areas of the tape were used to set the spot evaluator to zero absorbance.

Known hydrogen sulfide concentrations in p.p.b. were prepared by use of a precalibrated permeation tube (O'Keeffe and Ortman, 1966) in a dynamic calibration system. The permeation tube was constructed from FEP Teflon tubing, 0.2-in. inside diameter, 0.5-in. outside diameter, and 5.25-in. long. The permeation rates were 0.31, 0.71, and 1.59 μg. H₂S per min. at 10°, 20°, and 30° C., respectively. The dynamic calibration system is shown in Figure 3. Purified nitrogen contained under pressure in a cylinder is metered through the temperature conditioning coil and over the gravimetrically calibrated hydrogen sulfide permeation tube. At the same time, dry air from the other cylinder was metered into the

mixing chamber to further dilute the gas stream. By adjustment of the flow rate of the diluent air and the temperature of the permeation tube, the desired H₂S concentrations in the p.p.b. range were produced.

Effect of Humidity and Reagent Composition

The mercuric chloride-urea reagent developed by Paré does not react appreciably with a dry H₂S sample (Figure 4). Use of glycerol in the reagent system greatly increases response to dry H₂S samples. This is probably due to the hygroscopic nature of glycerol, which creates a humidified reaction media. At about 50% relative humidity created by passage of the gas sample through the humidifier, there is little difference in reactivity in reagents with and without glycerol. If the humidifier were to malfunction, however, as might happen during unattended field sampling operation, use of glycerol in the reagent would be advantageous because meaningful data would still be obtained. For this reason, a reagent containing glycerol was used in all experimental work reported in this paper and is recommended for similar work.

Test gas[a]	Previous exposure to H_2S		Subsequent exposure to H_2S	
	H_2S added, p.p.b.	H_2S found, p.p.b.	H_2S added, p.p.b.	H_2S found, p.p.b.
NO_2	6.3 ± 0.5^b	6.3 ± 0.6^b	9.9 ± 0.4^b	10.2 ± 0.2^b
SO_2	3.5 ± 0.4	3.3 ± 0.6	9.8 ± 0.2	9.6 ± 0.3
NH_3	7.0 ± 0.7	7.7 ± 0.3	9.9 ± 0.6	10.2 ± 0.7
CH_3SH	7.5 ± 0.3	1.3 ± 0.7	9.8 ± 0.4	1.4 ± 0.2
CH_3-S-CH_3	16.8 ± 0.7	16.7 ± 0.9	9.8 ± 0.5	9.8 ± 0.4
$CH_3-S-SCH_3$	14.9 ± 0.7	15.5 ± 0.6	9.8 ± 0.5	10.1 ± 0.4
Cl_2	7.0 ± 0.7	3.9 ± 0.5	9.8 ± 0.4	7.9 ± 0.7

[a] Exposure conditions: 10 p.p.m., sampled at 0.25 c.f.m. for 15 min.
[b] One standard deviation.

Range, Sensitivity, Precision, and Linearity

A calibration curve was constructed (Figure 5) from data obtained by use of the permeation tube and the dynamic dilution system as a primary standard source of p.p.b. concentrations of hydrogen sulfide. Each point on the curve represents the average of ten determinations. The average variation about the mean at the one standard deviation level was ±0.011 absorbance or about 0.5 p.p.b. These measurements were made on sections of tape selected at random from several different rolls; therefore, the data on precision of calibration curve given above include the effect of tape variability.

To determine the variability in absorbance of the blank tape, over 100 readings of various sections of tape were made. The standard deviation was ±0.009 absorbance indicating that the lower limit of detection of the method for a 2-hr. sample collected at 0.25 cu. ft. per min. is 0.5 p.p.b. The upper limit at these sampling conditions is 15 p.p.b.

The 2-hr. sampling method was calibrated by subjecting the prepared tape to higher concentrations of H_2S (in p.p.10 m.) for from 1 to 10 min. and extrapolating the absorbance to 2-hr. concentrations. The slope of the calibration curve (Figure 6) is comparable to the slope in Figure 5. Apparatus used for producing these controlled H_2S concentrations is shown in Figure 7. The major difference between this system and the one used for producing p.p.b. concentrations of H_2S is the elimination of the second dilution stage and use of a three-way solenoid valve and timer. These data indicate that the upper limit of concentration measurable can be extended considerably by reducing sampling time because the calibration curve is not affected significantly by sampling time and concentration over the range of time and concentration studied. Also indicated is that an accurate calibration curve in p.p.b. can be prepared by extrapolating values obtained from standard samples in p.p.10m.

Stability of $HgCl_2$ Tape

Stability of both undeveloped and developed tape was investigated. Stability of the exposed but undeveloped tape was determined over a 7-wk. period. Tapes exposed to approximately 7 p.p.b. H_2S were stored in plastic bags at room temperature. Six replicate samples were developed and read periodically. No decay trends were observed (Figure 8).

Stability of tape exposed to H_2S and developed with NH_4OH is shown in Figure 9. The tape was exposed to room air during the 8-day storage period. The decay rate is most rapid during the first 24 hr. These data indicate that if the tape is developed and read within the same working day, the decay

would be less than 2%. Redevelopment with ammonia returns the samples to their original density.

Interferences

Possible interference from seven gases was investigated. Test gases were introduced for 15 min. at a concentration of 10 p.p.m. and a flow rate of 7 liters per min. by use of a motorized syringe for metering the pure gas. Cylinder N_2 was used as a diluent. These gases were passed through tapes that were previously and subsequently exposed to hydrogen sulfide (Table 1). Methyl mercaptan and chlorine were the only gases that interfered. Methyl mercaptan interference is accompanied by the production of a yellow stain. None of the gases studied produce a measurable stain with the impregnated tape in the absence of H_2S.

Since methyl mercaptan is commonly present in atmospheres rich in hydrogen sulfide, further investigation into the magnitude of this interference was conducted. Several concentrations of methyl mercaptan were introduced on a tape previously exposed to 15 p.p.b. H_2S for 2 hr. Methyl mercaptan interference becomes noticeable at an H_2S to mercaptan ratio
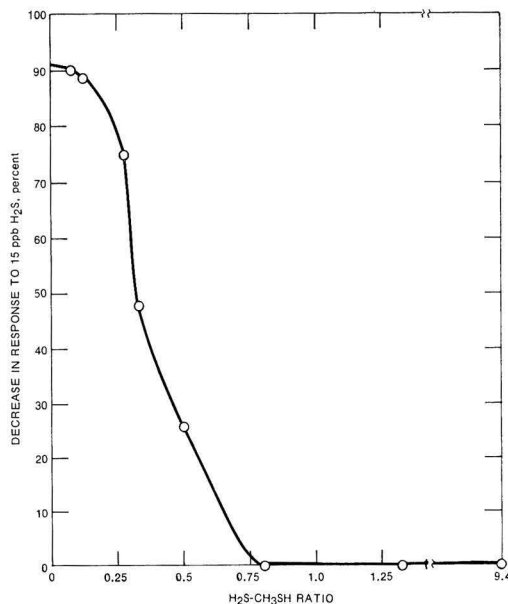
Figure 10. Interference of methyl mercaptan

Figure 11. Hydrogen sulfide levels in Cincinnati
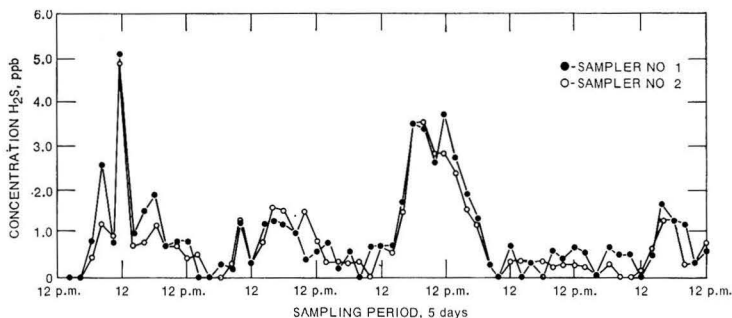
of less than 0.75. A ratio of 0.5 causes a 25% decrease in response. No mercaptan interference is noted when the H_2S to mercaptan ratio is greater than 1. Because the atmospheric concentration of H_2S is usually greater than that of CH_3SH, interference from CH_3SH would not ordinarily pose a problem. Interference from chlorine is not considered serious because chlorine levels in the atmosphere are generally below the level that would cause interference (Figure 10).

Reproducibility of Instrumental Method

Two tape samplers were operated simultaneously for 5 days in Cincinnati, Ohio, under field operating conditions to determine the reproducibility of the instrumental method. Data obtained are plotted in Figure 11. The average difference in 2-hr. concentrations over the 5-day period was calculated to be 0.09 p.p.b. with a standard deviation of ± 0.30 p.p.b., which is within the experimental error of the method.

Conclusions

The results obtained indicate that the mercuric chloride paper tape method can be used for measurement of H_2S in the range of concentration normally encountered in air pollution studies. The sampling instrumentation used has the advantages of low cost and simplicity of operation and maintenance.

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Ultraviolet Spectrophotometric Determination of Nitrite–Nitrate in KOH

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■ A method for the simultaneous ultraviolet spectrophotometric determination of NO_2^- and NO_3^- in aqueous KOH was developed. The molar absorptivities of NO_2^- and NO_3^- at the analytical wavelengths of 301 and 356 nm. are solvent dependent; the absorptivities of NO_2^- and NO_3^- at 301 nm. decrease linearly with KOH concentration; the absorptivity of NO_2^- at 356 nm. increases linearly with KOH concentration. Accurate analyses require the correct molar absorptivities and the KOH concentration must be known. Equations for the determination of NO_2^- and of NO_3^- are presented which require the determination of KOH concentration and the absorbances of the nitrite–nitrate in 1-cm. cell at 301 and 356 nm. The method was applied successfully to synthetic solutions, ranging from 0.5 to 7 *M* in KOH.

The most prominent air pollutants containing nitrogen are NO and NO_2; the ratio of NO to NO_2 emitted from automobile exhausts is generally 99:1 (Campau and Neerman, 1966). The methods that have been used for quantitatively determining this NO are: mass spectroscopy (Campau and Neerman, 1966), nondispersive infrared analysis (Huls and Nickol, 1967), oxidation to NO_2 (Nicksic and Harkins, 1962; Singh, Sawyer, *et al.*, 1968), gas chromatography of NO is also plausible (Dietz, 1968). This laboratory has been studying the possibility of determining NO by absorption in KOH solution according to the equation (Taylor, 1960):

$$4NO + 2OH^- \rightarrow N_2O + 2NO_2^- + H_2O \qquad (1)$$
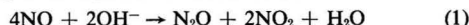
and then analyzing for nitrite using absorption spectroscopy. A similar method has been applied to NO_2 (Altshuller and Wartburg, 1960):

$$2NO_2 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O \qquad (2)$$
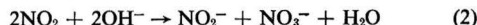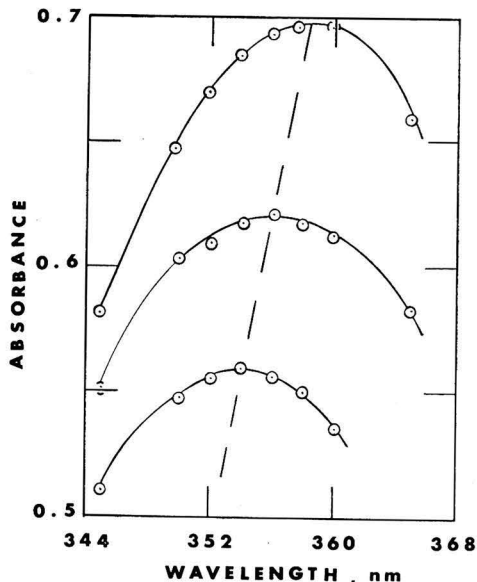
Figure 1. Hypsochromic shift of 0.03 M nitrite at KOH concentrations of 0 (highest absorbance), 4.9 M, and 8.5 M (lowest absorbance)

Figure 2. Molar absorptivities of nitrite and nitrate $vs.$ KOH concentration. Left ordinate is at 301 nm. Right ordinate is at 356 nm.

Reaction 2 is also investigated. These reactions and the possibility of simultaneously determining NO and NO₂ have required a study of the electronic absorptions of nitrite and nitrate as functions of wavelength, temperature, possible effects of nitrite–nitrate interactions upon absorption characteristics, and KOH concentration. These electronic absorptions were found to be significantly dependent upon the KOH concentration, and analysts who may use this absorption technique for NO₂ should have access to these data while our investigation of Reaction 1 is continuing.

Results and Discussion

Wavelength. The nitrate ion in aqueous solution shows electronic absorption bands centered at about 301 and 203 nm. with molar absorptivities of about 7,000 and 9,500 l./mol. cm., respectively. The higher wavelength maximum used here is solvent dependent (Rotlevi and Treinin, 1965) but does not shift wavelength here with KOH concentration up to 9 M, the highest concentration investigated.

The nitrite ion in aqueous solution shows electronic absorption bands centered at about 356, 280, and 210 nm. with molar absorptivities of about 23,000, 9,000, and 47,000 l./mol. cm., respectively. These bands are also solvent dependent (Strickler and Kasha, 1963). There is a hypsochromic shift of the high wavelength band as the KOH concentration is increased as shown in Figure 1. All subsequent measurements were made arbitrarily at 356 nm. No effect was noted on the much broader 280 nm. band. The 210 nm. band was not investigated.

Temperature. The absorption of the nitrogen oxides by KOH solutions was investigated at several temperatures, and the possible effect of change in solvent structure upon electronic absorption was studied. No temperature effects were evident in our experimental range, 25° to 45° C.

Nitrite–Nitrate Interactions. Since the projected simultaneous analyses required the molar absorptivities of nitrite and nitrate in the presence of each other, possible interaction effects were investigated. The solutions of Table 1 were pre-

pared and absorbances were measured $vs.$ distilled water and also $vs.$ the nitrite or nitrate blank of Table 1. The constancy of $A_{KNO_3}^{301}$ as nitrite is increased (column 4, upper half) and $A_{KNO_2}^{301}$ as nitrate is increased (column 4, lower half), indicates no measurable interference effects.
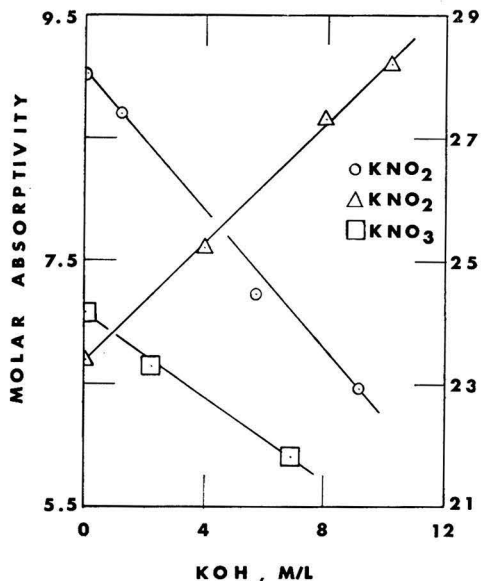
KOH Concentration. The effects of KOH concentration upon nitrite and nitrate molar absorptivities are significant as shown in Figure 2. The plots are linear and follow the equations:

$$\epsilon_{301}^{KNO_3} = 7.09 - 0.18 \, (KOH) \tag{3}$$

$$\epsilon_{301}^{KNO_2} = 9.02 - 0.28 \, (KOH) \tag{4}$$

$$\epsilon_{356}^{KNO_2} = 23.4 + 0.48 \, (KOH) \tag{5}$$

Although much data are available on the effects of different solvents on the energy (wavelength) and intensity of these absorptions of nitrite (Strickler and Kasha, 1963) and nitrate

Table I. Investigation of Possible Effects of Nitrite–Nitrate Interactions upon Electronic Transition at 301 nm.

1	2	3	4
			A_{301}
KNO₃ (M/l.)	KNO₂ (M/l.)	Solvent blank	Nitrate
0.0197	0	0.150	0.165
0.0197	0.0120	0.246	0.153
0.0197	0.0360	0.445	0.138
0.0197	0.0600	0.650	0.151
			Nitrite
0	0.360	0.330	0.315
0.0197	0.360	0.459	0.315
0.0591	0.360	0.700	0.320
0.0985	0.360	0.970	3.316

Table II. Simultaneous Ultraviolet Spectrophotometric Analyses of Synthetic Nitrite–Nitrate Solutions

KOH (M/l.)	$\epsilon^{301}_{KNO_2}$ (l./M cm.)	$\epsilon^{301}_{KNO_3}$ (l./M cm.)	$\epsilon^{356}_{KNO_2}$ (l./M cm.)	KNO$_2$ (M/l.)		KNO$_3$ (M/l.)	
				Added	Found	Added	Found
0.468	8.89	7.03	23.3	0.0240	0.0236	0.0591	0.0586
0.936	8.75	6.92	23.8	0.0120	0.0120	0.0393	0.0397
1.40	8.62	6.84	24.1	0.0360	0.0361	0.0197	0.0203
1.87	8.49	6.75	24.2	0.0240	0.0244	0.0787	0.0805
3.74	7.95	6.41	25.2	0.0240	0.0248	0.118	0.117
4.41	7.77	6.29	25.5	0.0240	0.0249	0.0591	0.0608
4.68	7.69	6.24	25.6	0.0120	0.0121	0.118	0.120
7.02	7.03	5.82	26.8	0.0360	0.0360	0.0393	0.0421

(Rotlevi and Treinin, 1965), our knowledge of the effects of solute–solvent interactions upon oscillator strength (and therefore absorptivities) is insufficient to rationalize the positive or negative trends of Figure 2. In any case the ultraviolet spectrophotometric determination of nitrite and nitrate, either separately or simultaneously, requires the determination of (KOH).

The method was applied to the simultaneous determination of nitrite and nitrate. Synthetic solutions were prepared. Absorbances at 356 and 301 nm. were determined as well as (KOH).

The nitrite is determined from the equation

$$(NO_2^-) = A_{356} \div [23.4 + 0.48 \, (KOH)] \qquad (6)$$

The nitrate is determined by rearranging Equations 3 and 4,

$$(NO_3^-) = \frac{A^{301} - \{(NO_2^-) \times [9.02 - 0.28 \, (KOH)]\}}{[7.09 - 0.18 \, (KOH)]} \qquad (7)$$

The application of this procedure is shown by the data for the synthetic solutions shown in Table II. The solutions are arranged in order of increasing (KOH) to emphasize the positive or negative effects upon the absorptivities. These effects of KOH are most important in the case of analyzing nitrate in the presence of nitrite in KOH solution; the failure to correct for (KOH) may contribute a large error to the calculation of Equation 7, if two relatively small numbers are involved.

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A Study of Jets of Electrically Charged Suspensions

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■ Experiments were conducted on jets of charged suspensions of glass and alumina particles. The Reynolds numbers based on the orifice diameter and gas velocity ranged from 300 to 3494. The charge to mass ratios were from 10^{-6} to 10^{-3} C. per kg. Even a small charge markedly altered the radial position of jet boundary of the particulate phase.

Processing streams in various air pollution control systems (Sargent, 1969) may take the form of jets of particulate suspensions. Knowledge of transport and diffusion of particulate matters in these jets is therefore useful in designs. In a gas these suspensions tend to become electrically charged by surface contact during handling or by collecting charges from an ionized gas (Soo, 1967). Hence, laminar and turbulent jets of suspensions of particles charged to various magnitudes were studied. They constitute unique examples of electrohydrodynamics (Soo, 1969a).

Experimental

For conducting experiments at conditions where Reynolds numbers based on orifice diameter were as low as 300, an orifice diameter of 0.1 in. was used. The jet chamber (1) and the blow-down system including the vacuum tank (2) and filter (3) for collecting particles are shown in Figure 1. The air flow through the orifice (5) and the dryer (13) was measured by a calibrated orifice meter (4); also shown is the probe holder with screws (7) for horizontal and (8) for vertical traverse. The belt-type particle feeder was driven by a motor (9), moving the particles from the hopper (10) through the gate (11) into the

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mixing chamber (12). An auxiliary jet of compressed air was used to assure removal of particles from the belt into the mixing chamber. The mixture was then transferred into the charging system in Figure 2, where a corona discharge from the point electrode to the grounded orifice was produced by a high voltage d.c. power supply (Del Electronics Corp.) connected for producing a negative corona. The onset voltage was 4.3 kV.

The velocity of the gaseous phase was determined with a pitot tube 0.021-in. i.d. This pitot tube was connected to a pressure transducer (Statham Instrument, Inc.). Its output into a bridge circuit was indicated on an electrometer (Keithley 610 RB) and recorder (Keithley).

The distribution of mass flow of the particle phase (glass particles of 35.5-μm. mean diameter of normal distribution, or alumina, 29 μm.) in the jet was determined by an isokinetic

sampling system given by Soo, Stukel, *et al.* (1969). For total flow of up to 2 g. per min, sampling probes of 0.32-in. and 0.07-in. i.d. were used. The overall flow was monitored by collecting it into a 25 × 80 mm. thimble (Whatman) at the bottom of the jet chamber. The chamber pressure was above − 2-in. water gauge in all the tests.

With particles of glass and alumina, particle charge was around 10^{-6} C. per kg. (we shall refer to this case as "uncharged") when the charging system in Figure 2 was replaced by placing the orifice and jet chamber (5) directly under the mixing chamber; with the system in Figure 2, but without applied voltage, 10^{-4} C. per kg. was acquired due to surface contact; and 10^{-3} C. per kg. was obtained with a corona voltage of 4.3 kV depending on the total feed rate (Figure 3). These charge-to-mass ratios were determined by measuring current from the above isokinetic sampling tube and dividing by the
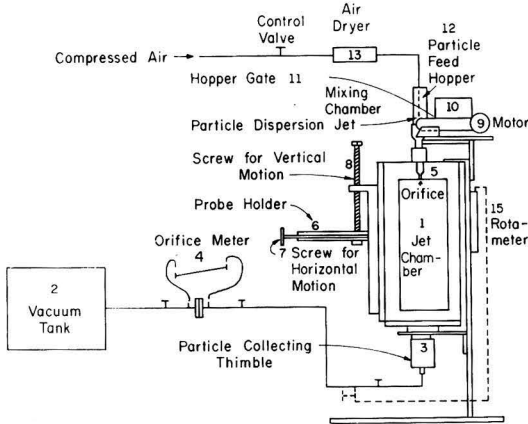
Figure 1. General layout of the system
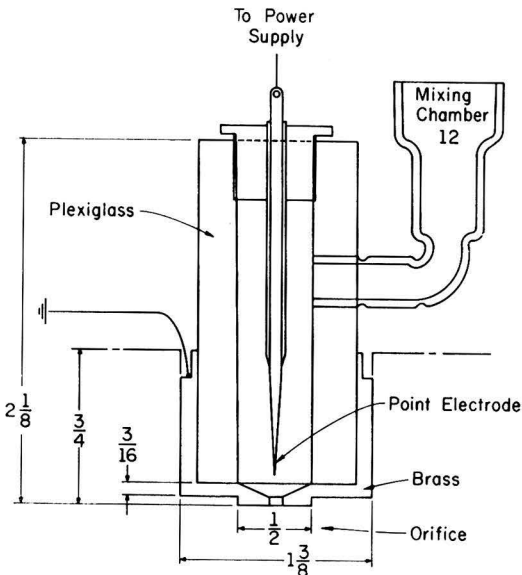
Figure 2. Details of corona charging system
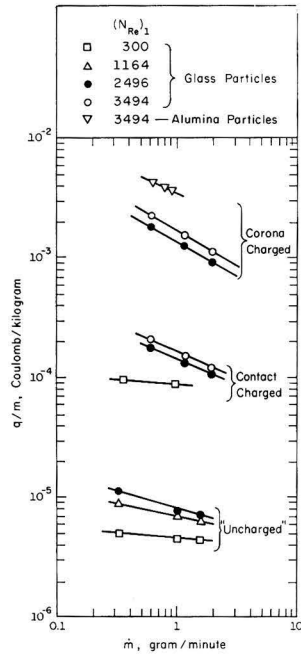
Figure 3. Charge-to-mass ratios of particles at various test conditions
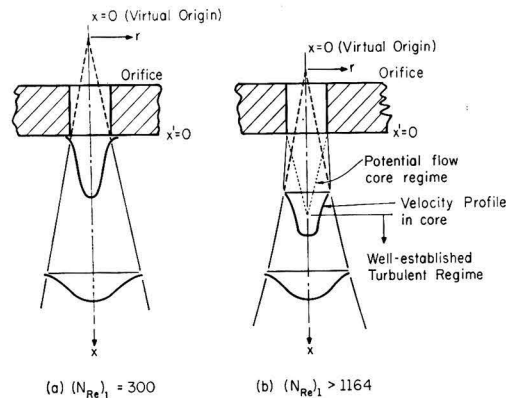
Figure 4. Flow regimes of gaseous phase in free jets

local mass flow. In this application, the isokinetic sampling tube acts as an electrometer, its metallic surface being a Gaussian surface; particles leaving the sampling tube were uncharged. Particle charges were also determined by placing a Faraday cage at the bottom of the jet chamber. In both cases the current (10^{-9} to 10^{-7} A) was measured by the above electrometer (Keithley).

Jet Configurations

Studies on jets of single phase fluids by Schlichting and Tollmien (see Schlichting, 1960) gave axial (coordinate x), velocity (u) distribution of jets far away from the orifice as:

$$u = D2\gamma^2/xX^2 \qquad (1)$$

Tollmien and others gave for turbulent motion $D = r_1u_1/\sigma$ where σ is an experimental constant between 35 (Schlichting, 1960) and 39 (Hinze, 1959; van der Hegg Zijnen, 1957); $D = \nu$ for laminar motion. The approximation of Görtler (1942) and Abramovitch (1963) gave:

$$u/u_o = \frac{1}{2}[1 + 0.125 (ar/x)^2]^{-2} \qquad (2)$$

the Reichardt's theory (Schlichting, 1960) gave:

$$u/u_o = \exp[-r^2/\Gamma x^2] \qquad (3)$$

These relations will be compared later with the results of the present study.

The coordinate x in the above relations measures from a virtual origin or source. Its relation to the location of the physical orifice is seen diagrammatically in Figure 4. For given mean velocity at the exit u_1, the velocity profile at the exit of the orifice depends on the length of the orifice giving, in the limit, fully developed pipe flow. The velocity distribution at the exit will follow a parabolic profile for fully developed laminar motion or a nearly 1/7th velocity prior to leaving the orifice for fully developed turbulent motion. Yet, we should expect slug flow for an ideal knife-edged orifice. Hence, it is reasonable to expect that for a physical system:

$$u_{o1} = k_u u_1 \qquad (4)$$

where $1 < k_u < 2$ and $k_u \sim 1$ for slug flow through the orifice and $k_u \gtrsim 2$ for laminar motion. Hence, the location of the exit of the orifice for the virtual origin is from Equation 1:

$$x_1 = \frac{\sqrt{3}}{2k_u}\gamma r_1 \qquad (5)$$

For turbulent motion, this represents the distance of the virtual origin to the end of the potential core (Figure 4), with $k_u \sim 1$. The range beyond the potential core is denoted as the well established turbulent region. Figure 5 shows the measured axial velocity with x' as the distance from the exit of the orifice. The curves are based on x_1 determined according to the procedure given next.

While transition to turbulence in the jet may take place at $(N_{Re})_1$ within 110 to 600, we found that the potential core existed above $(N_{Re})_1 = 1164$ (Figure 6). The location of the virtual origin was also confirmed by plotting x'/r_1 vs. b_u/r_1 (Figure 7). The spreading coefficient is denoted by c_u:

$$b_u/r_1 = c_u(x/r_1) \qquad (6)$$

The fluid jet boundary is given by:

$$(2/\sqrt{3})\gamma r_1/x = \xi_s^2/X_s \qquad (7)$$

Distributions in the fluid phase were not influenced by the
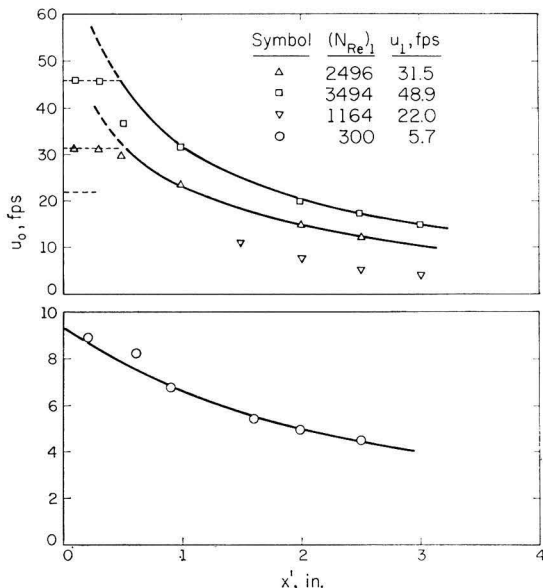
Figure 5. Centerline axial velocity of gaseous phase—curves show correlation from virtual origin (Fig. 7)
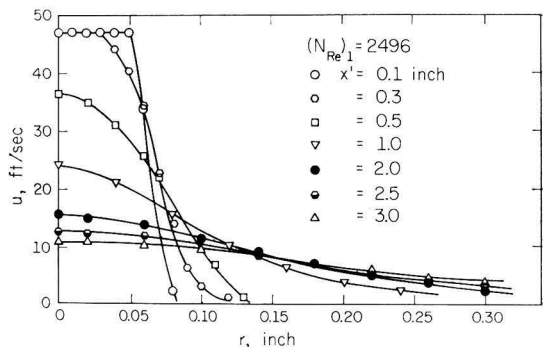
Figure 6. Gaseous phase velocity distributions at $(N_{Re})_1 = 2496$
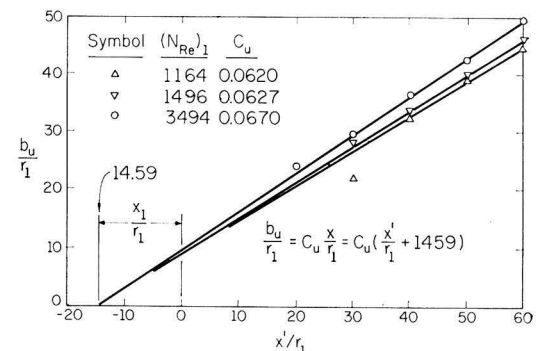
Figure 7. Location of virtual origin based on half-width (velocity) of the gaseous phase

presence of particles in the present study of dilute suspensions.

Since the relaxation controlled range of the jet is extremely short, our concern will be mainly the diffusion controlled range of the far jet condition.

Distributions of density of the particulate phase were given by:

$$\frac{\rho_p}{\rho_{p1}} = \beta_1 \frac{r_1}{x} [h_0(X) + x^* h_1(X) + x^{*2} h_2(X) + \ldots] \quad (8)$$

where $h_0(X)$ is known and β_1 is given by:

$$\beta_1 = \frac{1}{8} \left(\frac{u_1 r_1}{D}\right) \frac{(1 + 2N)}{(1 - X_{ps}^{-2N-1})} \quad (9)$$

The total mass throughput is:

$$\dot{m} = \pi \rho_{p1} r_1^2 u_1 = 2\pi \int_0^{r_{ps}} \rho_p u_p r \, dr$$

$$= 8\pi \beta_1 \rho_{p1} r_1 D \int_1^{X_{ps}} (h_0 + x^* h_1 + x^{*2} h_2 + \ldots) X^{-2} dX \quad (10)$$

The parameter x^* is given by:

$$x^* = [(q/m)^2 \tau/\gamma^2 D_p \epsilon_0] \beta \rho_{p1} r_1 x$$

$$= \frac{2}{3} (1 - X_{ps}^{-2N-1})^{-1} \left(\frac{\rho_{p1}}{\epsilon_0} (q/m)^2 \frac{r_1^4}{D_p^2}\right) \times$$

$$\left(\frac{D_p \tau}{r_1^2}\right) \left(\frac{r_1 u_1}{\nu}\right)^{-1} (D/\nu)(1 + 2N) \frac{x}{r_1}$$

$$\equiv \frac{2}{3} (1 - X_{ps}^{-2N-1}) N_{ev} N_{DF} (N_{Re})_1^{-1} (D/\nu)(1 + 2N) \frac{x}{r_1}$$

$$(11)$$

Figure 10. Mass flux density distributions of particulate phase (charged and uncharged glass beads) at $(N_{Re})_1 = 300$, $\dot{m} = 1.12$ g./min., $x' = 0.2$ in.
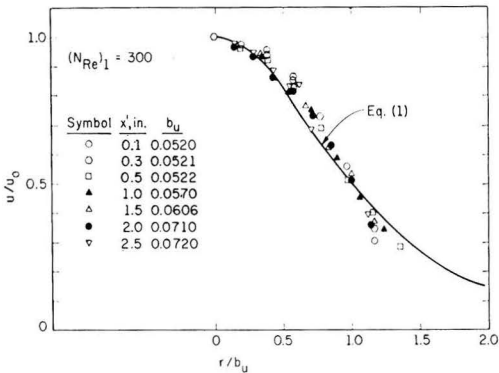
Figure 8. Gaseous velocity distributions in initial laminar jet
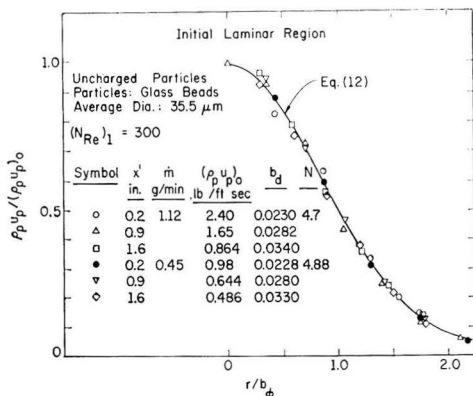
Figure 9. Mass flux density distributions of particulate phase (uncharged glass beads) in the initial laminar region at various feed rates
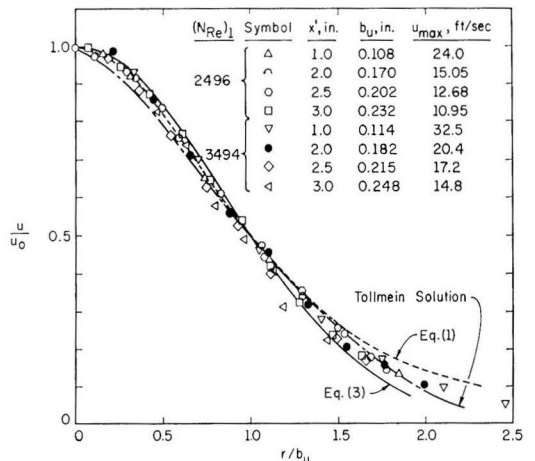
Figure 11. Gaseous phase velocity distributions in the well established region

$(N_{Re})_1$	$\dot{m}$g./min.	q/m (C./kg.)	N_{ev}	N_{DF}	x' (in.)	N	x^*
"Uncharged particles"[a]—laminar regime							
300	1.12	4.6×10^{-6}	0.1092	0.0113	2.0	4.7	3.65×10^{-3}
300	0.45	5.0×10^{-6}	0.0557	0.0113	2.0	4.88	1.85×10^{-3}
Contact charged particles							
300	1.12	9.0×10^{-5}	41.74	0.113	0.2	4.7	1.3999
					0.9		1.7781
					1.6		2.198
					2.3		2.662
300	0.45	9.5×10^{-5}	20.15	0.113	0.2	4.88	0.671
					0.9		0.851
					1.6		1.059
					2.3		1.267
"Uncharged particles"—well established regime							
2496	0.5	9.8×10^{-6}	8.1×10^{-6}	2.25	2.0	0.675	3.33×10^{-5}
2496	1.12	7.8×10^{-6}	1.4×10^{-5}	2.25	2.0	0.675	5.77×10^{-5}
Corona charged glass particles, 35.5 μm.							
2496	0.5	1.795×10^{-3}	0.02501	2.250	2.0	0.675	0.1031
					2.5		0.1223
					3.0		0.1416
					3.5		0.1608
2496	1.12	1.2×10^{-3}	0.02501	2.250	2.0	0.675	0.1032
					2.5		0.1225
					3.0		0.1417
					3.5		0.1610
3494	0.5	2.24×10^{-3}	0.01081	3.61	2.0	0.61	0.0699
					2.5		0.0830
					3.0		0.0960
					3.5		0.1091
2496	1.12	1.5×10^{-3}	0.01081	3.61	2.0	0.61	0.0702
					2.5		0.0833
					3.0		0.0965
					3.5		0.1096
Corona charged alumina, 29.5 μm.							
3494	0.5	4.0×10^{-3}	0.05228	4.2919	2.0	1.1	0.2200
					2.5		0.2612
					3.0		0.3024
					3.5		0.3435
3494	0.89	3.0×10^{-3}	0.05234	4.2919	2.0	1.1	0.2204
					2.5		0.2604
					3.0		0.3027
					3.5		0.3439

[a] Particles: glass beads, average diameter: 35.5 μ.

Equation 11 defines the electro-diffusion number N_{ev} (electrostatic force per diffusive force), diffusion response number N_{DF} (relaxation time per diffusion time) in addition to $(N_{Re})_1$ and the Schmidt number N.

Since the difference between the velocity of the particle phase and that of the gas is extremely small in the diffusion controlled range of the jet, u_p approximately equals u. The mass flow of the particle phase is therefore given by:

$$\frac{\rho_p u_p}{\rho_{p1} u_1} = \frac{1}{4} \left(\frac{\gamma r_1}{x} \right)^2 \frac{2N+1}{(1 - X_{ps}^{-2N-1})} \frac{1}{X^2} \times$$
$$(h_o + x^* h_1 + x^{*2} h_2 + \dots) \quad (12)$$

This relation was applied to correlating experimental data, which, in turn, gave us the density distribution of particles. Equation 12 also gives the Schmidt number from experimental results.

Results

Measured velocity distribution of the gaseous phase showed that an initially laminar jet of $(N_{Re})_1 = 300$, correlated well in the dimensionless plot of u/u_1 vs. r/b_u, b_u being the half-width, as shown in Figure 8. Comparison to the Schlichting solution given by Equation 1 shows that the agreement is excellent especially at axial locations further downstream. The mass
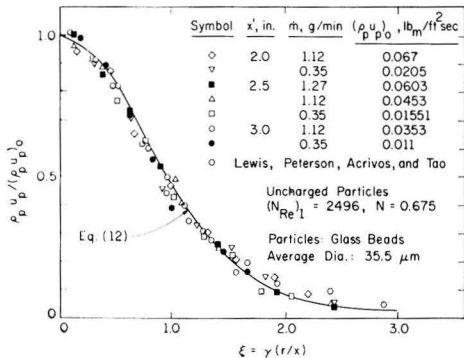
Figure 12. Mass flux density distributions of particulate phase (uncharged glass beads) at $(N_{Re})_1 = 2496$
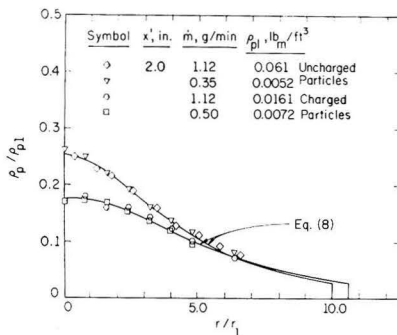
Figure 15. Concentration distributions of particulate phase (charged and uncharged glass beads) at $(N_{R.})_1 = 2496$, $x' = 2.0$ in.
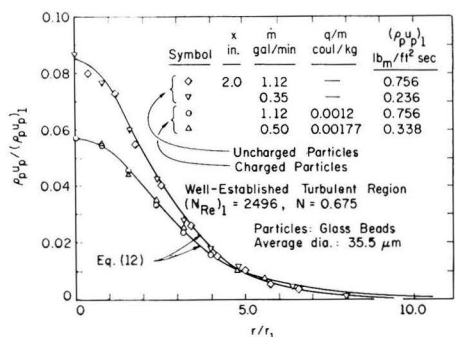
Figure 13. Mass flux density distributions of particulate phase (charged and uncharged glass beads) at $(N_{Re})_1 = 2496$, $x' = 2.0$ in.
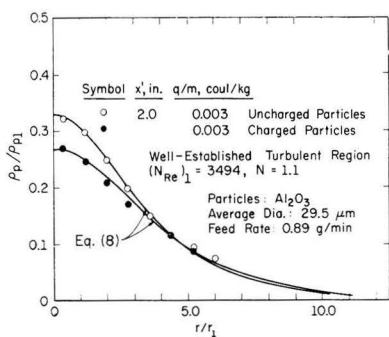
Figure 16. Concentration distributions of particulate phase (charged and uncharged aluminum oxides) at $(N_{Re})_1 = 3494$, $x' = 2.0$ in.
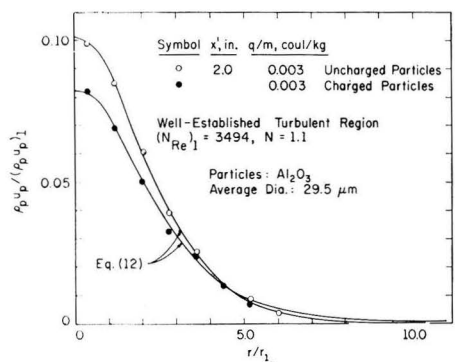
Figure 14. Mass flux distributions of particulate phase (charged and uncharged aluminum oxides) at $(N_{Re})_1 = 3494$, $x' = 2.0$ in.
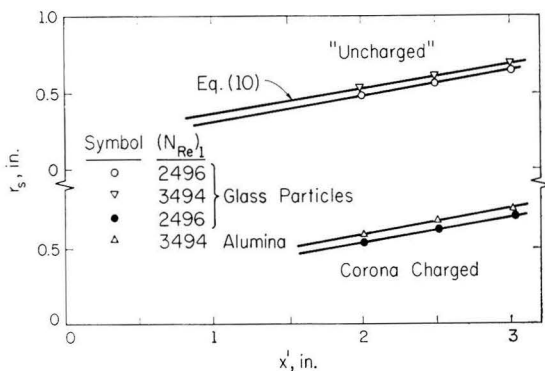
Figure 17. Jet boundary of the particulate phase

flow distribution in the uncharged suspension is given by

$$\Phi = \frac{\rho_p u_p}{\rho_{po} u_o} = \left(1 + \frac{1}{4}\xi^2\right)^{-2(N+1)}$$

from Equation 12.

The result is given in Fig. 9 together with Equation 12. The case of charged suspension in comparison to uncharged ($\sim 10^{-6}$ C. per kg.) is shown in Figure 10. The spread of the

particle jet boundary due to charge is seen. Experiments on $(N_{Re})_1 = 300$ are summarized in Table I.

In the well established turbulent regime at large $(N_{Re})_1$, the velocity distribution of the gaseous phase is as shown in Figure 11 for the cases $(N_{Re})_1$ of 2496 and 3494 with u/u_o plotted $vs.$ r/b_u. The velocity profiles as given by Equations 1 and 3 are also shown. At least near the jet axis, Equation 1 with Tollmien diffusivity gives the closest description of velocity.

The mass flow distributions of uncharged glass particles at $(N_{Re})_1 = 2496$ are illustrated in Figure 12 including a comparison to the data of Lewis, Petersen, et al. (1961). The actual mass flow distribution based on $(\rho_p u_p)/(\rho_{p1} u_1)$ for charged and uncharged glass particles at $(N_{Re})_1 = 2496$ is shown in Figure 13. The case of alumina suspension at $(N_{Re})_1 = 3494$ is illustrated in Figure 14. Their corresponding density distributions based on the fluid phase velocities are shown in Figures 15 and 16. Experiments on turbulent jets are summarized in Table I. Figure 17 gives a comparison of jet boundary with and without charges on particles.

Discussion

Comparison with trends of experimental data shows that correlations by Equations 1 and 12 are valid, and the idea of virtual origin is applicable to particulate suspensions.

The data showed that observable portions of the jet were principally diffusion controlled. The effect of particle diffusivity was indicated by the Schmidt number which for glass particles has the value of 4.7 and 4.88 for a laminar jet. The Schmidt number was much smaller in the well established turbulent regime of a turbulent jet, values of 0.61 and 0.675 were obtained for the suspensions of glass particles; a value of 1.1 was obtained for alumina particles because of greater density (3.97) of alumina particles in spite of its smaller average size compared to glass particles (density 2.2).

Diffusion of particles occurs due to fluid–particle interaction (Soo, 1969b). In laminar flow, diffusion of the particulate phase occurred due to its random motion produced by Brownian motion, fluid–particle interaction, and perturbation of the flow field by the particles. However, the average size of the particles used in this study was above 27.0 μ, and the diffusion of the particles due to Brownian motion was negligible. Photographic records showed that diffusion of the particulate phase on its jet boundary occurred throughout the entire region of turbulent motion of the jet.

When the fluid was in turbulent motion particles were set in random motion with r.m.s. relative velocity $(\Delta u^2)^{1/2}$, relative to the fluid. For a relaxation time, τ, an interaction length, L_p, is defined by $L_p = \tau (\Delta u^2)^{1/2}$. Due to the basic specifications, $\rho_p \ll \rho$, particle–particle collision was negligible. Therefore, with the gaseous phase in turbulent motion, the random motion of the particulate phase was uncorrelated, and the particles behaved like a rarefied gas even though the gaseous phase did not. When the interaction length was large compared to the characteristic dimension of the flow system, streaming of particles within the jet boundary was expected. This character of a particulate suspension was somewhat analogous to that of molecules in a rarefied gas.

The jet boundary of the particulate phase in the initial laminar region was limited to that of the gaseous phase based on the conservation of mass. At low Reynolds numbers particles charged by surface contact with the wall were sufficient to exhibit the effect of the electric field. When these particles were charged in a corona discharge, most of the particles were attracted back to the grounded ring electrode which formed the tip of the nozzle and no satisfactory measurements were possible. In this case the viscous force is overshadowed by the electrostatic attractive force between the positive electrode and negatively charged particles and the relations given by Equation 8 are no longer applicable.

The perturbation parameter, x^*, was a function of the axial coordinate, x, the electro-diffusion number N_{ev}, the diffusion response number, N_{DF}, the Reynolds number $(N_{Re})_1$, and the Schmidt number N. Results have shown that even a small

charge on the particles altered the jet spread considerably, pointing out the possibility of a hybrid type of dust collectors using both charge and jet actions.

Nomenclature

a = a constant
b_u = half-width of a jet or distance from axis where $u/u_o = 1/2$
b_Φ = half-width at $\Phi = 1/2$ ($b_\Phi = 0.00764\, x$ for $\dot{m} = 1.12$ g. per min.)
c_u = spreading coefficient
D = diffusivity of the fluid phase; equal to its kinematic viscosity, ν, for laminar motion and eddy diffusivity for turbulent motion
D_p = diffusivity of the particles
k_u = orifice velocity constant
$\dot{m}$ = total flow rate of particles
N = Schmidt number D/D_p
N_{DF} = diffusion response number
N_{ev} = electro-diffusion number
$(N_{Re})_1$ = Reynolds number of the orifice
q/m = charge to mass ratio of the particles
r = radial coordinate
r_1 = radius of the orifice
r_s = radius of the jet boundary of the fluid
r_{ps} = radius of the jet boundary of the particle phase
u = axial velocity of the fluid phase
u_1 = mean velocity at the orifice
u_o = maximum axial velocity at a given x
u_p = particle velocity
x = axial coordinate from virtual origin
x_1 = location of orifice from virtual origin
x' = location from orifice
x^* = a dimensionless perturbation parameter
X = $1 + (1/4)\xi^2$
X_s = $1 + (1/4)\xi_s^2$
X_{ps} = $1 + (1/4)\xi_{ps}^2$
β_1 = coefficient for distribution of particle density
γ = $(\sqrt{3}/8)(2 r_1 u_1/D) = (\sqrt{3}/8)(N_{Re})_1$
Γ = an empirical constant
ϵ_o = permittivity of free space (m.k.s. system of units)
ν = kinematic viscosity of fluid material
ξ = $\gamma r/x$
ξ_s = $\gamma r_s/x$
ξ_{ps} = $\gamma r_{ps}/x$
ρ_p = density of particulate phase
ρ_{p1} = mean density of particles at the exit of the orifice
ρ_{po} = maximum density of particles at a given x
σ = an experimental constant
τ = relaxation time for momentum transfer from fluid to particles
Φ = $\rho_p u_p/\rho_{po} u_o$

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COMMUNICATIONS

Reactions of O₂¹Δg with Olefins and Their Significance in Air Pollution

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■ The relative importance to air pollution of the reactions of olefins and other unsaturated organic compounds with atomic oxygen or molecular oxygen in its lowest-lying excited state is assessed in terms of recent experimental data. It is concluded that reactions of excited molecular oxygen are less important than the corresponding atomic oxygen reactions.

Table I. Rate Constants for Some Reactions of O³P and O₂¹Δg

Reactant	k, cm.³ mol.⁻¹ sec.⁻¹		$k(O^3P)/k(O_2{}^1\Delta_g)$
	O³P	O₂¹Δg[a]	
Ethylene	4×10^{11}[b,c,d]	$\leq 1 \times 10^7$	4×10^4
Propene	2×10^{12}[e,f,g]	$\leq 1 \times 10^7$	$\geq 2 \times 10^5$
1-Butene	2.5×10^{12}[b,f,g]	$\leq 1 \times 10^7$	$\geq 2.5 \times 10^5$
Isobutene	1×10^{13}[b,f,h]	. . .	. . .
2-Butene	1×10^{13}[b,f]	$\leq 1 \times 10^7$	$\geq 1 \times 10^6$
2-Methyl-2-butene	4×10^{13}[i]	$\leq 1 \times 10^7$	$\geq 4 \times 10^6$
2,3-Dimethyl-2-butene	5×10^{13}[i]	1.0×10^9	$\geq 5 \times 10^4$
2,3-Dimethyl-2-pentene	. . .	7.0×10^8	. . .
3-Hexyne	. . .	$\leq 1 \times 10^7$	. . .
1,3-Pentadiene	. . .	$\leq 1 \times 10^7$	. . .
1-Methylcyclopentene	. . .	1.5×10^7	. . .
1,2-Dimethylcyclopentene	. . .	4×10^8	. . .
1,2-Dimethylcyclohexene	. . .	4×10^8	. . .
1,3-Cyclohexadiene	. . .	9×10^7	. . .
1,4-Cyclohexadiene	. . .	$\leq 1 \times 10^7$	. . .
Benzene	4×10^{10}[j]	$\leq 1 \times 10^7$	$\geq 4 \times 10^3$
o-Xylene	7×10^{11}[j]	$\leq 1 \times 10^7$	$\geq 7 \times 10^4$
2,5-Dimethylfuran	$\leq 10^{14}$[k]	1.6×10^{10}	$\leq 6 \times 10^3$

[a] Herron and Huie, 1969
[b] Elias, 1963
[c] Westenburg and deHaas, 1969
[d] Niki, Daby, *et al.*, 1969
[e] Moss and Jennings, 1968
[f] Cvetanovic, 1959
[g] Saunders and Heicklen, 1966
[h] Smith, 1968
[i] Cvetanovic, 1960
[j] Mani and Sauer, 1968
[k] Estimated

The possible importance of O₂¹Δg in photochemical air pollution has been discussed in two recent papers (Pitts, Khan, *et al.*, 1969; Kummler, Bortner, *et al.*, 1969). The latter have suggested that the rate constants for the reactions of O₂¹Δg with olefins are comparable to the rate constants for the reactions of O³P with olefins. This, if true, would make O₂¹Δg reactions far more important for olefin loss in the atmosphere than O³P reactions.

To support this suggestion, Kummler, Bortner, *et al.* (1969) point out the similarity in rate constants for the reactions of O₂¹Δg and O³P with O₃ and O₂⁻. As further evidence, they cite the work of Falick, Mahan, *et al.* (1965) on the reactions of O³P and O₂¹Δg with ethylene.

The argument based on comparison of rate constants is not compelling, but the observations of Falick, Mahan, *et al.* (1965) cannot be dismissed. They found that for discharged oxygen (which contains approximately equal amounts of O³P and O₂¹Δg), addition of sufficient ethylene to consume completely all the O³P had no effect on the O₂¹Δg concentration. On the other hand, if sufficient NO₂ was first added to consume all the O³P, then the addition of a small amount of ethylene caused the O₂¹Δg to disappear.

These experiments were interpreted by Mahan (1969) to mean that the rate constants for the reaction of O³P and O₂¹Δg with ethylene were similar. While the second set of experiments might lead to such an interpretation, the first set clearly indicates that O³P is much more reactive than O₂¹Δg.

This may be illustrated by considering the relevant rate expressions

$$O + C_2H_4 \rightarrow \text{Products}$$

$$O_2{}^1\Delta_g + C_2H_4 \rightarrow ?$$

for which (neglecting the stoichiometry of the atomic oxygen reaction)

$$\frac{d(O)}{d(O_2{}^1\Delta_g)} = \frac{k_1(O)}{k_2(O_2{}^1\Delta_g)}$$

or

$$\frac{k_1}{k_2} = \frac{\log[(O)_o/(O)_t]}{\log[(O_2{}^1\Delta_g)_o/(O_2{}^1\Delta_g)_t]}$$

the subscripts o and t defining initial and final concentrations.

The ratio k_1/k_2 can be estimated by making reasonable guesses as to the sensitivity of the experiment. Thus, if 1% of the oxygen atoms is not consumed, and 5% of the $O_2{}^1\Delta_g$ is consumed, then $k_1/k_2 = 100$. If 10% of the atomic oxygen is not consumed, and 10% of the $O_2{}^1\Delta_g$ is consumed, then $k_1/k_2 = 20$. This is almost certainly a lower limit to this ratio.

This difference in reactivity is supported by the observations of Elias (1963). He found that the rate constant for the reaction of atomic oxygen with ethylene was the same over a wide range of temperature whether or not the reaction was studied in the presence of $O_2{}^1\Delta_g$.

These interpretations are confirmed by recent work in our laboratory on the direct measurement of $O_2{}^1\Delta_g$ rate constants (Herron and Huie, 1969).

In Table I we summarize our rate measurements and give rate constants for relevant O^3P reactions for comparison. If reaction rate is taken as the index of importance, then the relative concentrations of $O_2{}^1\Delta_g$ to O^3P must be at least 10^4 for $O_2{}^1\Delta_g$ to be as important as O^3P in photochemical air pollution. [Findlay, Fortin, et al. (1969) have found a deacti-

vation rate constant for benzene of 3.2×10^6 cm.^{3} mol.$^{-1}$ sec.$^{-1}$ This makes $k(O^3P)/k(O_2{}^1\Delta_g) \geq 1 \times 10^4$.] Clearly, as long as the relative concentrations of oxygen allotropes are in the approximate range of $O_3 = 1$, $O_2{}^1\Delta_g = 10^{-6}$, and $O^3P = 10^{-8}$ (Kummler, Bortner, et al., 1969), the reactions of $O_2{}^1\Delta_g$ with the compounds studied cannot make more than a minor contribution.

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Selenium in Papers and Tobaccos

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■ The selenium contents of a number of types of papers and of some tobaccos are reported. The selenium contents of the papers were low, generally less than 0.05 p.p.m. Pipe and cigarette tobaccos contained a little more selenium than the papers, ranging from 0.03 to 0.13 p.p.m. Cigar tobaccos contained somewhat more, ranging from 0.33 to 1.01 p.p.m.

W est and Cimerman (1964) have described a micro-determination of selenium by the ring oven technique. This method is sensitive to 0.1 microgram of selenium. Using it, they found 22 varieties of filter paper to contain substantial amounts of selenium, some as much as 2 micrograms in a circle of 22-millimeter diameter.

Later (*Chem. Eng. News*, 1967), it was reported that with this method selenium was found in relatively large amounts in cigarette papers (about 10 parts per million) and in lesser

amounts (2–4 p.p.m.) in tobaccos from cigarettes made in the U.S. Significant amounts were reported as found in most other kinds of papers. A relationship between the selenium in paper and lung cancer and emphysema was suggested.

Selenium has not been found associated with plant cellulose. Thus, the high selenium content of papers as reported above was surprising. In view of the report by Kubota, et al. (1967) the results for tobaccos also appeared higher than should be expected for crops from the tobacco-growing areas. It was felt, therefore, that the selenium content of paper and tobacco should be further investigated, using other methods of analysis.

Materials

Cigarette papers were obtained either in packages of the "roll-your-own" type or by removing them from cigarettes purchased at the market. They were cut into small sections with scissors for analysis.

Office and other types of paper were taken from supplies purchased through normal market channels. They were ground through a 2-mm. screen with a Wiley mill.

Pipe tobaccos and cigars were purchased at the market, cut into small pieces with scissors and analyzed without drying.

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Method of Analysis

Analyses were made on 1.0-g. samples by the method of Watkinson (1966) with minor modifications (Olson, 1969).

Results and Discussion

The results of the analysis of papers are summarized in Table I. The highest average value for selenium was found with corrugated cardboard. It is quite possible that this is because of selenium in the glue used in the manufacture of this paper. All of the other papers had selenium contents which fell near the lower limit of reliability of the method, about 0.02 p.p.m. The values are much lower than the 10 p.p.m. in cigarette paper, 1.4 p.p.m. in bond writing paper, 0.7 p.p.m. in mimeograph paper, 1.2 p.p.m. in paper towels, 6.5. p.p.m. in glossy magazine print, and 4 p.p.m. in newsprint found by the ring oven technique (*Chem. Eng. News*, 1967).

The results of the analysis of some tobaccos are shown in Table II. Here, again, the values are considerably below the 2–4 p.p.m. reported by the ring oven technique (*Chem. Eng. News*, 1967). However, they are higher than values for selenium for paper in this study. In view of the association of selenium with protein in plants (Rosenfeld and Beath, 1964), this seems logical. Further, the data for tobaccos are in good agreement with the data for crops in the tobacco-raising areas of the United States (Kubota, *et al.*, 1967).

The method used in this work has been subjected to a collaborative study and has been compared to five other methods for the analysis of plant materials (Olson, 1969). It has performed well in both cases. Included in the methods with which it was compared were neutron activation analysis and the method of Allaway and Cary (1964), with which the oxidation of samples takes place in a closed vessel, thus minimizing chances for the loss of selenium during this step. In view of this, it would seem that the method used here should give satisfactory results on paper and tobacco. Nevertheless, the great differences between the results obtained here and those obtained by the ring oven technique made further study of paper advisable.

Three samples of cigarette paper were submitted to two outside laboratories and were also analyzed as a part of this study. One laboratory (J. L. Martin, Colorado State University) could detect no selenium in these papers using a colorimetric method based on diaminobenzidene (Cummins, *et al.*, 1965). The other (W. H. Allaway, Soils, Plant, and Nutrition Laboratory, ARS-USDA) found well below 0.1 p.p.m. of selenium in the papers by a fluorometric method (Allaway and Cary, 1964).

One of the authors (D. V. Frost) used a colorimetric method (Cummins, *et al.*, 1965) to analyze five samples of glossy magazine print of the kind found by the ring oven technique to contain 6.5 p.p.m. of selenium (*Chem. Eng. News*, 1967). No selenium could be detected, although the method is capable of easily detecting the amount found by the ring oven technique.

Using a method essentially that of Ewan, *et al.* (1968), but omitting the arsenic coprecipitation, one of the authors (D. V. Frost) could not detect selenium in a composite of four 22-cm. circles of filter paper (one each from Whatman No. 1 and No. 3 and Schleicher and Schuell No. 410 and No. 589) in three separate trials. No selenium was detected in 200-mg. samples of glossy magazine print. However, 0.1 μg. of selenium as the selenite added to either a composite of the filter papers or to the glossy magazine print was recovered.

Finally, a sample of cigarette paper which had been found to contain 0.02 p.p.m. of selenium by the method used in this study was submitted for neutron activation analysis without radiochemical separation (Gulf General Atomic). Selenium was not definitey detected in the sample. A long-lived gamma-ray photopeak was observed about where ^{75}Se would be expected. If we assume it was selenium, the paper would have contained not more than 0.14 p.p.m. of selenium.

In view of the above analytical results, it appears that papers and tobaccos contain considerably less selenium than previously reported.

Table I. Selenium Content of Papers

Type of paper	Samples analyzed	Selenium content (p.p.m.) Range	Av.
Cigarette ("roll-your own" type)	8[a]	0.01–0.05	0.03
Paper from cigarettes	6[b]	0.01–0.06	0.02
Office-type papers	13[c]	0.00–0.06	0.02
Brown paper towels	3	0.02–0.03	0.02
Corrugated cardboard	2	0.05–0.13	0.09
Filter paper	2		0.00
Cleansing tissue	1		0.00
Magazine print, glossy	1		0.01
Newsprint	1		0.03
Brown wrapping paper	1		0.04

[a] Four different brands included in this number.
[b] All from different brands of cigarettes.
[c] Includes nine different kinds of papers commonly used in offices.

Table II. Selenium Content of Tobaccos

Kind of tobacco	Number of brands analyzed	Selenium content (p.p.m.) Range	Av.
Tobacco from cigarettes	9	0.03–0.13	0.08
Pipe tobacco	7	0.08–0.09	0.08
Tobacco from cigars			
Wrap, binder, and filler	7	0.33–1.01	0.50
Wrap and binder only	3[a]	0.22–0.37	0.31
Filler only	3[a]	0.36–0.88	0.65

[a] Wrap and binder for three different brands and filler for same brands.

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industry trends

Texaco Trinidad, Inc., a subsidiary of Texaco, Inc., will construct a 90,000 barrel per day desulfurization plant at its refining center at Point-a-Pierre, Trinidad. The low sulfur fuel oil will help supply East Coast U.S. markets.

Combustion Engineering, Inc. (Windsor, Conn.), has been awarded a $13 million contract by Electric Energy, Inc. (Joppa, Ill.), to install electrostatic precipitators on six coal-fired steam generators. The precipitators will operate at 98.6% efficiency.

The M. W. Kellogg Co. has been awarded a $291,000 contract by the National Air Pollution Control Administration. Kellogg will provide NAPCA with engineering and applied research services for one year; the contract has a two-year renewable clause.

Pall Trinity Micro Corp. (Cortland, N.Y.), will build sewage treatment plants for a new series of naval fighting ships. Pall will receive $1.5 million over four years under subcontract to the main shipbuilding contractor, Litton Industries.

The Warner Co. (Philadelphia, Pa.), has acquired the stock of several Pennsylvania and New Jersey companies in the solid waste management field. Included are Penn Sanitation Co. and Waste Automation Corp. The acquisition is part of a move by Warner to expand its environmental and reclamation division.

Trans Union Corp. has set up a new company—Ecodyne Corp.—to bring together eight companies in the water and waste water treatment field. One of the eight companies is Graver Water Conditioning Co. Ecodyne will have annual sales in excess of $50 million.

Allis-Chalmers (Milwaukee, Wis.), will install its first commercial Bio-Disc waste water treatment process in a Wisconsin cheese factory this summer. The Bio-Disc process employs aerobic bacterial attack on organic waste constituents.

The Ben Holt Co. (Pasadena, Calif.), and **Harold C. Spaetgens Engineering, Ltd.** (Calgary, Alberta), have jointly formed Holt Engineering, Ltd., a new firm which will offer engineering, consulting, and other services. The new firm will specialize in cold weather plant design and pollution control facilities.

The International Nickel Co. of Canada, Ltd., plans to construct a 2300 ton per day sulfuric acid plant at its Copper Cliff (Ont.), nickel complex. The plant will recover sulfur dioxide from smelter gases and will be the largest of its type in the world.

The Foxboro Co. will spend $250,000 on a waste treatment plant at Foxboro, Mass., to prevent pollution of nearby Neponset Lake. The company also has received state approval for its $100,000 treatment plant at East Bridgewater, Mass., on stream since June 1969.

Chemical Construction Corp. (CHEMICO) will design and build the first large-scale SO_2 removal and recovery installation for the Boston Edison Co. in Massachusetts. The project represents a breakthrough in both commercial acceptance of the concept and in cooperation between various sectors of industry and government. Cost of the project is estimated at $5 million to be equally divided between Boston Edison and the National Air Pollution Control Administration. The scrubber to be installed will clean a gas volume of *ca.* 450,000 a.c.f.m. Also, it has been. estimated that the SO_2 removed from stack gases will suffice to fill feedstock requirements of the Essex sulfuric acid plant (50 tons per day output) which CHEMICO will utilize as a recovery unit.

Gulf Oil Corp. announced recently the birth of Gulf Energy and Environmental Systems, Inc., in San Diego, Calif. The new company fulfills Gulf's earlier promise to commercialize its nuclear fuel and power plant equipment for environmental control.
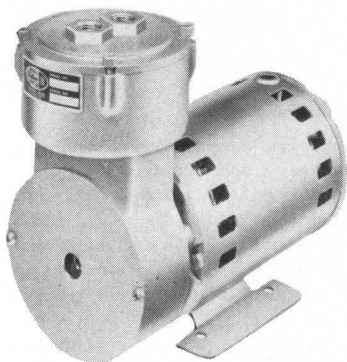
Bellows pump/compressor

Bellows activated vacuum pump/compressor designed specifically for continuous duty contaminant-free operation. Compressors with explosion proof motors able to operate under hazardous conditions. Pump is able to accept small amounts of liquid at constant flow which creep through filtration systems. Metal Bellows Corp. **61**

Hydrocarbon extraction

A test kit for rapid, accurate determination of Freon-extractable hydrocarbons has been developed. For oil concentrations under 500 p.p.m a 1-liter sample is taken (an aliquot is used for higher concentrations) and extracted twice with Freon TF. The solvent is driven off by heat, and the last stage of the evaporation is carried out in a specially shaped calibrated glass vessel that permits direct reading of volumetric oil concentration after the Freon is gone. Kit includes: glassware, hot plate, filter paper, ring stand, reagents. Nalco Chemical **62**

SO_2–NO_2 analyses

A continuous sampling colorimeter has been developed that automates the accepted chemical methods of analyses for sulfur dioxide and nitrogen dioxide. Unit converts from SO_2 to NO_2, or the reverse, in 10 min. Variable range: 0.5 to 8.0 p.p.m. full-scale. Zero drift—less than 1% over 24-hr. periods. Automatic zero and photometer

calibration every 24 hr. Complete with rotary, disk-type scrubber, independent liquid and air flow system, dual-beam colorimeter with vertical flow cells, and motor driven optical chopper, the Waco Air Analyzer is suitable for use with any electronic recorder with 0 to 100 mV input and suitable input impedance. Wilkens-Anderson Co. **63**

Computer data system

The Symetrics Automatic Data Acquisition system (SADAQ-II) automatically interrogates remote monitoring stations and initiates supervisory commands with total control up to 128 remote locations with 128 sensors or local commands at each site. For application from process control to environment pollution monitoring, or from measurement of hydrometeorological data to control of utility systems. Under total control of a central computer, it recalibrates sensor zero points, alarms the operator of out-of-tolerance conditions, and, if desired, initiates corrective action. Symetrics Engineering Corp. **64**
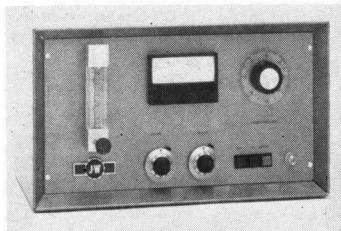
CO analyzer

Model US400L is designed to measure the carbon monoxide content in the ambient air. The operation is based on the reaction of carbon monoxide in the presence of mercury oxide at elevated temperature, causing the generation of mercury vapor. The mercury vapor is passed through an atomic absorption chamber, where the concentration is evaluated in terms of carbon monoxide present in the air sample. The measuring range is 0–50 p.p.m. CO in air. Bacharach Instrument Co. **65**

Air monitor

An SO_2 analyzer for air pollution monitoring with a measuring range of 0–5 p.p.m and a response speed of 30 sec. is adaptable to laboratory or field use and can operate unattended for up to 8 days. Operating principle is based on electroconductivity, using a flow of distilled water; since no chemical reagents are required, maintenance is at a minimum. Operates on 115-V, 60-cycle source or 12-V d.c. Bacharach Instrument Co. **66**

Conductivity meter

Battery operated conductivity meter has four-position switch for selecting scales from 0–50 to 0–50,000 μmhos. Gives linear readout on all scales. One epoxy dip-type cell, which is automatically temperature compensated, operates over the entire range. Factory calibrated. Has internal checkpoint for instant standardization. Aquatronics, Inc. **67**

Stack afterburner

A new thermal oxidation system is aimed at control of hydrocarbon or organic solvent emissions from a broad range of manufacturing processes. Each unit is custom designed, and utilizes controlled burning at proper conditions of time, temperature, and turbulence. Acrometal Products, Inc. **68**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

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automated colorimetric analysis of SO₂ and NO₂

Waco's Air Analyzer is truly a continuous sampling colorimeter, automating the accepted chemical methods of analysis for sulfur dioxide and nitrogen dioxide providing: reliability... highest quality components used throughout.

Designed for continuous operation with flexibility... convert from SO₂ to NO₂ in 20 minutes. Variable range, from 0.5 to 4 ppm full scale. Zero drift... less than ±3% in 7 day periods. Automatic zero and photometer calibration every 24 hours.

For complete information, contact:

Chlorine monitor

The Chlorometer is an accurate all solid-state electronic process controller and measuring instrument sensitive to chlorine in aqueous solutions. Measures from 0 to 20 p.p.m. chlorine with other ranges available measuring from 1 to 1000 p.p.m. chlorine full-scale. Designed for water treatment plants, water pollution control, food processing, chemical manufacturing, electronic manufacturing, and industrial cleaning systems. Delta Technical Laboratories   **69**

Waste flow recorder

Constructed of noncorrosive fiber glass laminates, epoxy resins, and simple parts for ease of maintenance, the Gravity Flow recorder produces a strip-chart record of the volume of sewage or drainage flow by the minute, hour, day, or month. Also provides a digital readout totalizer. Models are available up to 1000 gal./min. with flume or in unlimited quantities without flume. Snyder Teague, Inc.   **70**

Filter holders

A new line of filter holders, suitable for handling all types of air sampling, is available with effective filter areas of 25, 35, and 88-mm. diameter in both open and in-line aluminum construction. Also, 25 and 35-mm. diameters in stainless steel. All holders have positive seals. Research Appliance Co.   **71**

Pollution study cage rack

A new laboratory animal cage bathes animals in a continuous flow of ambient air or a stream of potentially harmful biologic environmental particulate matter enabling study of the effects of such pollutants upon animals. The compact, portable, self-contained unit is engineered to provide economical and effective operation. Becton, Dickinson, and Co.   **72**

Water filtration

Inexpensive filtering medium of thin series of vertical "sheets" of compacted sand proves to be more efficient than the conventional sand filter, removing solids down to 1μ without addition of coagulating chemicals or precoat materials. Embodied in a corrosion-proof system, this filter has shown up to 99.8% solids removal. Bohna Engineering and Research, Inc.   **73**

Dilution system

The instrument provides accurately diluted samples for analysis by particle counting or gas analyzing instruments that will not use excessive concentrations. Effective for diluting samples with particles 5 μ or smaller from power plant, heating system, chemical process stacks, or other sources with turbulence, it provides a continuous supply of cooled, dilute gas. Changes in analyzer system flow rate up to 0.5 c.f.m. will not affect dilution ratios. Royco Instruments, Inc.   **74**

Stream sampler

The model 1260 stream selector permits sequential sampling of up to 10 liquid or gas streams. Electric loads of up to 5 A can be handled by each of the 10 available channels. Motor driven valves assure positive sealing up of each sample stream. Union Carbide Corp.   **75**
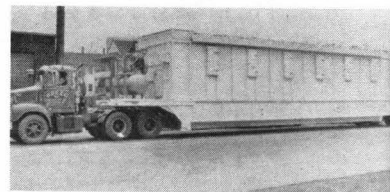
Dust collector

The new Model P Porta-Kleen dust collector will filter 64,000 cu. ft. of exhaust gases per min. removing up to 12,000 pounds of rock dust per hour. Its use easily permits portable asphalt plants to meet the most stringent air pollution control requirements. The completely portable unit can be moved from site to site by a standard truck tractor, and comes complete with ICC running lights, brakes, and other accessory equipment for easy mobility. Flex-Kleen Corp.   **76**
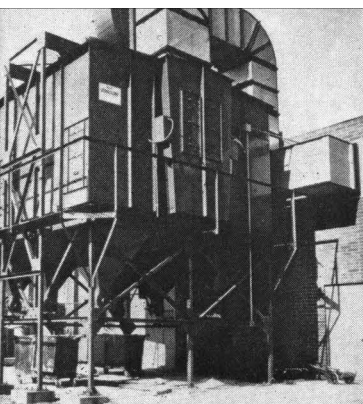
In-building air cleaner

The Multi-Seal Dynaclone avoids plant heat loss and the need for makeup air by exhausting cleaned process air inside buildings. The filter's low velocity collection prevents bag wear without sacrificing efficiency. Handling 24,000 and 34,000 c.f.m., respectively, the filters collect dust, abrasive particles, and trap materials. Filter classifiers capture heavy particulate; cloth bags collect lightweight fines. A choice of modern filter fabrics permits handling a multitude of applications and temperatures to 250°F. W. W. Sly Mfg. Co. **77**

Incinerator system

A new dual-chamber incinerator system features an electrically operated loading door with built-in safety interlock that prevents overloading and assures efficient combustion of solid wastes and emission of smoke, odor, and visible fly ash within accepted standards. Available in five standard sizes capable of disposing 300 to 1500 lb. of Class 0 and Class 1 wastes per hour. Environmental Control Products, Inc. **78**

Dust scrubber

Containing modular foam bed stages, the HS Wheelabrator Turbex wet dust collector scrubs dust laden air in operations such as foundry sand systems and cupola melting furnaces, asphalt dryers, rubber reclamation plants, mine crushers, and lead oxide mixers. Can handle 1600 to 105,600 c.f.m. Construction features include a controlled-rate flushing system, perforated collector plates, and a full length entrainment separator. Wheelabrator Corp. **79**

Cleaning Our Environment The Chemical Basis For Action

Cleaning Our Environment—The Chemical Basis for Action is the highly acclaimed 249-page report based on a three-year study by the Subcommittee on Environmental Improvement of the ACS Committee on Chemistry and Public Affairs. Leading experts from the fields of chemistry, biochemistry, chemical engineering, biology, entomology, and other disciplines comprised the Task Force on Environmental Improvement which conducted the study, one of the most comprehensive of its kind.

The report divides the problem of environmental improvement into four parts: air environment, water environment, solid wastes, and pesticides. It clearly shows where extensive fundamental research is required to provide a better working understanding of the environmental system. Focusing strongly on chemistry, chemical engineering, and related disciplines, the report concludes that the U.S. possesses enough technical know-how to take enormous strides now toward a cleaner environment.

Included in the report are 73 recommendations for action on such topics as:
- *flow, dispersion, and degradation of water and air pollutants*
- *short- and long-range effects of water and air pollutants*
- *municipal and industrial waste water treatment*
- *advanced treatment processes*
- *eutrophication*
- *air quality criteria*
- *air monitoring systems*
- *emission control on motor vehicles*
- *abatement of pollutants from power plants*
- *municipal and industrial solid wastes*
- *mining and processing wastes*
- *pesticides and human health*
- *pesticides and wildlife*
- *methods of pest control*

Although the ACS report is directed primarily at technical and nontechnical administrators in the environmental field, research managers, legislators and others working in this area, the nature of the subject makes it required reading for all scientists interested in environmental problems and their solutions.

The report is available from the ACS Special Issues Sales. Price: $2.75.

new literature

Filtration system. Bulletin 802E describes a twin chamber filtration system which can be used for filtration of corrosive liquids. The filament reinforced epoxy system can handle 5000 gallons per hour and can be used for acids, alkaline plating solutions, and other corrosive industrial effluents. Sethco Manufacturing Corp. **91**

Water scrubber. Bulletin B-770 describes water jet eductor venturi scrubber for removal of mists, dusts, and gases. The scrubber can also be used to recover valuable products from effluents in various industries including the chemical, metal finishing, refining, electroplating, and fertilizer industries. Heil Process Equipment Corp. **92**

Reducing SO_2 control costs. Abstract discusses minimizing costs of equipment necessary to convert existing systems to operate on low sulfur fuels as opposed to installing purification control units in the exhaust system. Walden Research **93**

Standards on SO_2 emission. A guide for regulation of the relationship among desired ground-level concentrations of sulfur oxides' pollutants, the dispersion capabilities of stacks, and the sulfur content of fuel burned in an indirect heat exchanger. American Society of Mechanical Engineers **94**

Sewage treatment. A 6-page bulletin describes sewage treatment by polymer flocculants. Chemical agents are effective in clarification, thickening, digesting, dewatering, and sludge pumping. Nalco Chemical Co. **95**

Sewage aeration. Bulletin describes single-stage centrifugal compressors for sewage aeration applications. Compressors are available in volumes from 5000 to 150,000 a.c.f.m. and heads from 5000 to 23,000 ft. and above. Allis-Chalmers **96**

Water monitoring and sampling. The 4-page catalog lists research and educational-type instruments for use in the marine environment at 30 to 100 meter depths. Monitoring instruments measure temperature, conductivity, dissolved oxygen, pH, and depth. Also, sampling devices for subsurface physical, chemical, biological, and geological investigations. Martek Instruments, Inc. **97**

Waste gas control. The Microjet spray scrubber is described concerning its ability to collect gas-borne particulates by atomizing water droplets and propelling them into the gas stream at high velocities, causing a violent mixing reaction and subsequent capture of the particles by the droplets. Its ability to remove sulfur and other chemical compounds from waste gases is displayed by graphs and charts. FECOR Industries, Ltd. **98**

Air analyzer. Bulletin No. 270 describes a continuous sampling colorimeter for SO_2, NO_2, and NO_x analyses. The analyzer provides automatic and continuous sampling of air samples. Wilkens-Anderson Co. **99**

Air sampler. Bulletin 193 describes a sampler which can be set for specified mass flow rates. The sampler maintains these flow rates despite changes in air temperature, barometric pressure, flow restriction, or pump efficiency. National Instrument Laboratories, Inc. **100**

Solid waste disposal. Bulletin RC-12870 describes the Radapactor compactor which reduces the volume of waste such as household garbage to 30% of its original volume. Bulletin RI 13070 describes the Mark VI-R Radicator incinerator, which accepts dry or wet solid waste, metal, glass, and the like. Midland-Ross Corp. **101**

Fume and vapor filtration. A 4-page bulletin describes features and advantages of fume and vapor filtration systems adaptable to pickling, cleaning, plating, and other industrial processes. Wean United, Inc. **102**

Smoke monitors. Bulletin No. 1004B describes smoke photoelectric density meters, alarms, and recorders for accurately monitoring smoke discharge and promoting efficiency of boilers, incinerators, and air ducts. Reliance Instruments Mfg. Corp. **103**

Atmospheric instrumentation. Literature describes equipment available for wind recording systems and direction control. In addition to the standard wind equipment and precipitation recorders, special equipment to suit specific needs can be supplied. Wong Laboratories **104**

Waste water analysis. Bulletin 9-33 discusses the complete line of waste water services available from Calgon. The 4-page publication relates the necessity of waste water analysis, the steps involved in such an analysis, and the significance of typical determinations which are run on water samples. Calgon Corp. **105**

Gamma and X-ray analysis. Literature describes an advanced single channel nuclear pulse height analyzer. Components included are amplifier, analyzer, six decode scalers, five decode timers, log ratemeter, linear ratemeter, and high voltage supply. Digital Automation Co., Inc. **106**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

Analytical standards. Bulletin 111 lists 46 kits for calibration, identification, and standardization of instruments such as gas chromatographs, spectrophotometers, and thin-layer and paper chromatography equipment. Polyscience Corp. **107**

Water pollution packet. "Pollution Control, a Kit for Concerned Citizens" is a general information packet on water pollution and the means available for its solution. The materials are designed to provide factual and current information for individuals and organizations concerned with the water pollution problem. Rex Chainbelt, Inc. **108**

Environmental instrumentation. The 28-page brochure describes and illustrates the many types of air and water environmental control applications which the company's broad line of sensors, analytical instruments, readout devices, controllers, and monitoring and telemetry systems can handle. Leeds & Northrup Co. **109**

Pollution control publications. "Quantitative Analysis of Gaseous Pollutants," "Chemical Detection of Gaseous Pollutants," "The Particle Atlas," "The Particle Analyst-Compiled," and "The Analysis of Air and Its Impurities" are five technical publications detailing areas of pollution. Ann Arbor-Humphrey Science Publ., Inc. **110**

Industrial noises. A miniature battery-operated sound-level meter, designed to measure industrial noises in accordance with national and international standards, is described in a new 6-page bulletin, which also lists a pocket-sized calibrator. Mine Safety Appliances Co. **111**

In-plant pollution control. Catalog 1450 illustrates Precipitron oil mist control units for eliminating in-plant air pollution in instances where as much as 10 gal. of cooling oil can be spread into the air in one 8-hr. shift in machine shops. Westinghouse Electric Corp. **112**

Industrial waste treatment. Literature describes DBC Plus Dried bacteria cultures being used successfully in treating petroleum in water bodies, animal and vegetable oils, greases in water, while demonstrating good capability in reducing phosphates in waste water. Gerald C. Bower, Inc. **113**

Tertiary water treatment plant. "Appraisal of Granular Carbon Contacting, Phase 3: Engineering Design and Cost Estimate of Granular Carbon Tertiary Waste Water Treatment Plant" contains the process description, design bases, plant operation, control rationale, equipment list and specifications, and cost estimate for a 10-million gal./day plant. Office of Information, Ohio Basin Region, Federal Water Pollution Control Administration, 4676 Columbia Pkwy., Cincinnati, Ohio 45226 (Write direct)

Waste water treatment. "Operation of Wastewater Treatment Plants" is written specifically for the operator and is updated to reflect changes and developments in waste water treatment

plant operational practices since the original publication. 200 Pages, $3.00. Water Pollution Control Federation, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016 (Write direct)

Solid waste fact book. A 24-page booklet describes solid waste and present status of disposal methods. It also describes the environmental pollution control program of the Glass Container Manufacturers Institute. Public Affairs Department, Glass Container Manufacturers Institute, Inc., 330 Madison Ave., New York, N.Y. 10017 (Write direct)

Instrumentation catalog. The 1970 edition of the "Honeywell Instrumentation Handbook" includes information on instrumentation and meteorology customer services. The 276-page catalog also includes definitions of technical terminology used in the instrumentation industry. C. F. Creswell, Honeywell Test Instruments Division, P. O. Box 5227, Denver, Colo. 80217 (Write direct)

Films

Water conservation. The film "Water" provides support for the water conditioning industry and demonstrates Morton's interest in and concern for water conservation. Recipient of nine honors, the film stresses conservation and the attempts to control and reduce pollution and examines future household, industrial, and recreational demands on water. Morton Salt Co., 110 North Wacker Dr., Chicago, Ill. 60606 (Write direct)

Air pollution. Professionally produced films illustrate the serious problem of air pollution and what to do about it. On loan free for group showing. National Medical Audiovisual Center (Annex), Station K, Atlanta, Ga. 30324 (Write direct)

Ecological problems. A series of 67 films show what's happening and what must be done to combat environmental threats facing the world today and in the future. Films may be rented or purchased. McGraw-Hill, 330 W. 42nd St., New York, N.Y. 10036 (Write direct)

bookshelf

Biological Conservation. David W. Ehrenfeld. xi + 226 pages. Holt, Rinehart, & Winston, 383 Madison Ave., New York, N.Y. 10017. 1970. $3.50, paper.

This book covers pollution and pollution control, characteristics of endangered species, population control, management of communities and species, and the hazards of present political, economic, and social policies. According to the publishers, the book is not written in an emotional vein, but "treats the fate of communities of plants and animals and of individual species in the modern world in an authoritative, straightforward, and uncompromising manner." ∎

An Introduction to Mathematical Ecology. E. C. Pielou. viii + 286 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1969. $14.95, hard cover.

A technical publication providing a background for those ecologists attempting to formulate and solve their problems by mathematical reasoning. Areas covered include population dynamics, spatial patterns, many species' spatial relations, and composition, diversity, and ordination of species communities. ∎

Earth Day–The Beginning. Compiled and edited by the National Staff of Environmental Action. 233 pages. Bantam Books, Inc., 666 Fifth Ave., New York, N.Y. 10017. 1970. $1.25, paper.

The highlights of the speeches and events that occurred during the nationwide Earth Week. Includes over 50 presentations made by students, scholars, scientists, and politicians. According to Bantam publishers, "this guide to survival focuses on the major threats to our environment and suggests ways in which groups and individuals can reverse the rush towards extinction." ∎

Water Supply and Treatment. 10th ed. By Merrill L. Riehl. xiii + 220 pages. National Lime Association, Washington, D.C. 20016. 1970. $3.50, hard cover.

The earlier editions of this book have been widely used texts on water treatment. Mr. Riehl discusses "water supplies and the methods by which water is treated to make it more useful and better adapted to human and industrial requirements." ∎

Environment and Plant Response. Michael Treshow. xv + 422 pages. McGraw-Hill, Inc., 330 W. 42nd St., New York, N.Y. 10036. 1970. About $11.50, hard cover.

Dr. Treshow, director of a PHS-sponsored air pollution graduate training program, describes, on both morphological and physiological bases, the roles of temperature, water, light, soil, and atmosphere on plant development. The book is valuable for courses in pathology, ecology, physiology, and horticulture and is also a reference for workers in the air pollution field, allowing diagnosis of plant disease associated with the physical environment. ∎

Population Resources Environment. Paul R. Ehrlich and Anne H. Ehrlich. 383 pages. W. H. Fre & Co., 660 Market St., San Francisco, Calif. 94104. 1970. $8.95, hard cover.

Dr. Ehrlich, a population biologist and ecologist, and his wife aim to give a comprehensive, detailed analysis of the worldwide crisis of overpopulation and the resulting demands on food, resources, and the environment. ∎

Environmental Geology: Conservation, Land-Use Planning and Resource Management. Peter T. Flawn. xix + 313 pages. Harper & Row, 49 E. 33rd St., New York, N.Y. 10016. 1970. $13.95, hard cover. ∎

Environment and Human Efficiency. E. C. Poulton. xxi + 328 pages. Charles C Thomas Publ., 301–327 E. Lawrence Ave., Springfield, Ill. 1970. $15.50, hard cover.

The book is practical and nontechnical with documented and illustrated material summarizing and interpreting recent research on human performance under environmental stress. The whole range of everyday environments is discussed with the evaluation of human efficiency. ∎

Proceedings of the Second Mineral Waste Utilization Symposium. vii + 373 pages. ITT Research Institute, P.O. Box 4963, Chicago, Ill. 60680. 1970. $15.00, hard cover.

This book gives "broad coverage and up-to-date techno-economic information in areas dealing with pollution and environmental problems." The symposium itself was planned in order to bring as much expertise as possible to bear on the problems involved with solid wastes. ∎

Chemical Fallout. Current research on persistent pesticides. Edited by M. W. Miller and G. G. Berg. xxii + 507 pages. Charles C Thomas, Springfield, Ill., 1969. Hard cover.

Proceedings of a conference on toxicity at the University of Rochester are arranged in a sequence that follows pesticides from their entry into ecological systems to their ultimate effect on human populations. An appendix reviews the procedures for registering new pesticide formulations. ∎

Scientific Circular 799–Final Technical Report on the Role of Solvents in Photochemical Smog Formation. Compiled from research at Battelle Memorial Institute. 46 pages. Technical Division, National Paint, Varnish, and Lacquer Association, 1500 Rhode Island Ave., N.W., Washington, D.C. 20005. 1970. $1.00, paper. ∎

August 10-14
Engineering Foundation of the United Engineering Trustees, Inc., and Committee on Engineering Manpower Development of the American Society of Civil Engineers
The Development of Environmental Managers

Henniker, N.H.

Conference deals with effective management of the various aspects of environmental control and the interfaces between public and private sectors and with government groups. Attendance is by application or invitation with fee of $160. Contact: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017.

August 16-19
Water Conditioning Association International
Water Conditioning Industry Exposition

Washington, D.C.

Silver anniversary of the industry features exhibits by suppliers of materials and services. Water problems and treatments to be discussed by government, press, engineers, educators, and members of Congress. For information and booth space: Gene Burton, WCAI Convention Committee, P.O. Box 651, 325 W. Wesley St., Wheaton, Ill. 60187

August 19 and 20
Water Research Council
Symposium on Water Pollution and Health

Washington, D.C.

All aspects of water supplies and contamination from the health standpoint will be covered. More information: David X. Manners, 237 E. Rocks Rd., Norwalk, Conn. 06851

August 23-29
World Health Organization and Pan American Sanitary Bureau
XII Interamerican Sanitary Engineering Congress

Caracas, Venezuela

Theme will be "Urban Sanitation." Papers will discuss habitat, water consumption, pollution, legislation, and sanitary standards. For details: Secretariat of the Organizing Committee of the Congress, Apartado 2006, Caracas, Venezuela.

August 24-26
Oak Ridge Associated Universities
Conference on Energy and the Environment

Oak Ridge, Tenn.

Will deal with the implications for the urban environment and natural resources of various alternative approaches to meeting the nation's future energy requirements. For information: W. W. Grigorieff, Special Projects Office, ORAU, P.O. Box 117, Oak Ridge, Tenn. 37830

August 24-28
Engineering Foundation and others
Application of Environmental R&D to Landfill Disposal for Solid Wastes

Deerfield, Mass.

Conference will deal with disposal and degradation of solid wastes in the landfill, improving efficiency of operations, site selection, ultimate use, and guidelines for sanitary landfills. Full details: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

September 1 and 2
American Management Association
Marketing Pollution Control Products

New York City

Presentations on marketing, profits, legislation effects, organization, regulations, and public relations of the pollution control industry. Contact: Vincent E. Schoeck, Pollution Control Division, The Carborundum Co., Hagerstown, Md. 21740

September 9
Agricultural Research Institute
Committee on Agriculture in Relation to the Quality of the Environment

Washington, D.C.

For details: Dr. T. J. Army, Research and Development, Great Western Sugar Co., P.O. Box 5308 PA, Denver, Colo. 80217

September 13-18
American Chemical Society
160th National ACS Meeting

Chicago, Ill.

Topics include: biochemical responses to environmental stresses; atmospheric reactions; air analysis and control technology; solid waste chemistry; organic matter in natural waters; thermal pollution; and "Earth Day in Retrospect." Complete details: *Chem. Eng. News*, June 29, 1970. Also, contact: Chicago Section, ACS, 86 E. Randolph St., Chicago, Ill. 60601

September 14-17
Association of Iron and Steel Engineers
Iron and Steel Exposition and Convention of Association of Iron and Steel Engineers

Cleveland, Ohio

Traditionally the steel industry's largest trade show, the Exposition will feature exhibits of pollution control-oriented devices and papers on pollution control at the technical meetings. Expected attendance is 15,000. Contact: Russ Robinson, Association of Iron and Steel Engineers, 1010 Empire Bldg., Pittsburgh, Pa. 15222

September 14-17
New Jersey Animal Waste Disposal Task Force
Agricultural Waste in an Urban Environment

Atlantic City, N.J.

First conference dedicated to finding a practical solution to the pressing national problems of agricultural waste. Will be special sessions on legislation, funding, research, and public relations. Write: Richard D. Chumney, New Jersey Dept. of Agriculture, P.O. Box 1888, Trenton, N.J. 08625

September 23-25
22nd Annual Convention and Operator's School, Western Canada Water and Sewage Conference
Winnipeg, Manitoba

For full information: D. A. Shillabeer, Rm. 324, Administration Bldg., 109th St. and 98th Ave., Edmonton 6, Alberta

September 29-October 2
U.S. Department of the Interior
Conference and Exposition on Environmental Pollution

Washington, D.C.

Will cover 18 major environmental topics in more than 50 sessions. Pollution abatement equipment, techniques, and services will be displayed. More than 3000 attendees expected. More information: Public Information Office, Interior Dept., 18th and C Sts., N.W., Washington, D.C. 20240

September 30-October 2
The University of Michigan and Michigan State University
International Conference on Environmental Mercury Contamination: Present Knowledge and Research Needs

Ann Arbor, Mich.

Participants will discuss distribution and transport of mercury in the environment and possible hazards associated with mercury exposures. Information: Conference Center, Extension Service, The University of Michigan, 412 Maynard Ave., Ann Arbor, Mich. 48104

meeting guide

October 4–9
Water Pollution Control Federation
43rd Annual Conference
Boston, Mass.
Over 250 exhibits of water pollution control equipment, supplies, and processes. Program includes management, collection, treatment, and research of industrial wastes, oil pollution, sludge disposal, and estuaries and coastal waters. Write: Editor, Water Pollution Control Federation, Room N-400, 3900 Wisconsin Ave., Washington, D.C. 20016

October 8 and 9
Mid-Atlantic Section of the Air Pollution Control Association and Vehicular Exhaust Committee of the National Air Pollution Control Association
Harrisburg, Pa.
Examination of the problems of transportation and air pollution. Information: William O. Farley, Director of Public Information. Consolidated Edison Co. of New York, 4 Irving Pl., New York, N.Y. 10003.

October 8 and 9
West Coast Section of the Air Pollution Control Association
Fifth Technical Meeting
San Francisco, Calif.
Theme will be "What's Next in Air Pollution?" Write: Sidney A. Mandel, Information Officer, Air Resources Board, 1108 Fourteenth St., Sacramento, Calif. 95814

October 28
New York State Action for Clean Air Committee
Symposium on Air Pollution and Respiratory Disease
Albany Medical College, Albany, N.Y.
Symposium will be cosponsored by several local tuberculosis and respiratory disease associations and will be chaired by Frank M. Woolsey, M.D., of Albany Medical College. Emphasis will be on conditions in New York State. For details: New York State Action for Clean Air Committee, 105 E. 22nd St., New York, N.Y. 10010

November 2–6
IUPAC, and the Federation of Swedish Industries
International Congress on Industrial Waste Water
Stockholm
The congress will deal exclusively with control of industrial water pollution by use of in-plant process changes or through waste water treatment. The program covers, one by one, the majority of industries with water pollution problems. Full details from: International Congress, Drottning Kristinas väg 47, S-114 28 Stockholm, Sweden

November 6–10
American Institute of Biological Sciences, and Federation of American Societies for Experimental Biology
First National Biological Congress
Detroit, Mich.
Theme of the congress will be "Man and Environment." Morning sessions will deal with scientific topics, but will appeal to both professional and layman. Evening symposia on the subject of man, environment, and public policy will bring together environmentalists and lawmakers. For full details: National Biological Congress, 3900 Wisconsin Ave., Washington, D.C. 20016

November 19 and 20
Center for Research in Water Resources, University of Texas
Conference on Conflicts in Water Resources Planning—What Are the Remedies?
University of Texas, Austin
The 2 day session will feature a series of lectures and papers concerning various aspects of the topics water, land, and people; government's role in water resources planning; and ecology as a planning parameter.

Courses

August 10–14
The Ohio State University
Short Course on Air Pollution Engineering
Columbus, Ohio
Topics include sampling, plant site selection, atmospheric reactions, design and specification of control devices, and emission standards. Registration fee is $225. For details: T. L. Sweeney, Chemical Engineering Dept., Ohio State University, 140 W. 19th Ave., Columbus, Ohio 43210

August 17–21
UCLA
Short Course on Fundamentals of Pollutant Formation in Combustion Processes
Los Angeles, Calif.
Will deal with combustion thermodynamics and rate processes as applied to combustion in mobile or stationary sources, modification of combustion conditions to minimize pollution, and treatment of exhaust gases. Fee is $310. Details: UCLA Extension, 10851 LeConte Ave., Los Angeles, Calif. 90024

August 18–20 (Boston)
August 31–September 2 (Los Angeles)
Technical Forum Associates
Short Course on Water Pollution Control
Will discuss sources, types, and effects of water pollutants; biological and chemical aspects; and changes in ecological patterns. Fee is $225. Write: R. S. Stone, Technical Forum Associates, Inc., 545 Technology Square, Cambridge, Mass. 02139

August 18–21
USDA, Forestry Service
Short Course on Tree and Forest in an Urbanizing Environment
Amherst, Mass.
Current information on effects of vegetation in a quality environment for people and problems encountered in managing this quality environment. Base fee $20 excluding lodging. Contact: Harold G. Marx, Northeastern Forest Experiment Station, 6816 Market St., Upper Darby, Pa. 19802

September 22–25
University of California
Short Course on Management of Solid Waste for Optimum Environmental Control
Berkeley, Calif.
Will deal with social, cultural, economic, and technological factors governing generation of solid wastes and with practical problems involved in proper management. Fee is $20. Write: Continuing Education in Engineering, University Extension, University of California, 2223 Fulton St., Berkeley, Calif. 94720

October 5–7
Cyrus Wm. Rice Division of NUS Corp.
Seventeenth Annual Water Seminar
Pittsburgh, Pa.
Seminars for management, engineering, and operating personnel with water management and quality control. Registration fee $300. Write: Cyrus Wm. Rice Division, NUS Corp., 1910 Cochran Rd., Pittsburgh, Pa. 15220.

(*Meeting Guide continued*)

October 12–16
University of California
Environmental Design and Risk Criteria in Offshore Operations
University of California, Berkeley
Course will demonstrate types of marine environmental data that can be obtained, how such data can be used, and what risks can be expected in marine operations. Registration fee is $225. For details: University Extension, University of California, Berkeley 94720

November 9–13
Vanderbilt University
Process Design in Water Quality Engineering
Vanderbilt University, Nashville
Seminar will cover design concepts and developed design problems in the areas of physical, chemical, and biological treatment of waste water, and sludge handling and disposal. Registration fee of $150 includes problem notebook. More information: W. W. Eckenfelder, Jr., Box 6222 Station B, Vanderbilt University, Nashville, Tenn. 37203

Institute for Environmental Technology and Occupational Safety and Health, Inc.
Correspondence courses for middle management industry personnel
Nine courses are now available: Introduction to air pollution problems; Water quality management; Use of radiation in industry; Industrial safety; Use of incineration in industry; Engineering methods for in-plant noise reduction; Industrial noise—the medical view; Measurement of hearing in industry; Environmental health legislation enacted during the 1960's. Full details from the institute at 1001 Connecticut Ave., N.W., Suite 701, Washington, D.C. 20036

Call for papers

March 7–11, 1971
Society of Toxicology
Annual Scientific Meeting of the Society of Toxicology
Aims to promote knowledge in toxicology and to exchange information among members and investigators of other sciences. Titles should be submitted to Dr. Wayland J. Hayes, Professor of Biochemistry, Vanderbilt University School of Medicine, Nashville, Tenn. 37203 no later than October 1, 1970.

April 19–22, 1971
Ohio State University
International Symposium on Livestock Wastes
Columbus, Ohio
Symposium on livestock wastes: their treatment, disposal, pollution properties, and handling. Abstract deadline is October 1, 1970. Contact: International Symposium on Livestock Wastes, c/o The Center for Tomorrow, Ohio State University, Columbus, Ohio 43210

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