

FEBRUARY 1978
ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T



**Toxic pollutants: current focus
in water pollution controls**
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Designed for maximum accuracy
in SO₂ sampling

NEW RAC 3-Gas Sampler

Unique thermoelectric cooling-heating system* assures optimum stability for SO₂ samples at ambient temperatures from -25°C to 50°C

Recent studies performed by the EPA have revealed that the accuracy of wet-chemical sulfur dioxide (SO₂) sampling procedures are adversely affected by high ambient temperatures. At 50°C (122°F), for example, roughly 75% of the SO₂ in a collected or stored sample will be lost (because of thermal instability) within a 24-hour period. Sample degradation begins in the 20°C (68°F) range, with an initial loss factor of less than 1% in 24 hrs.

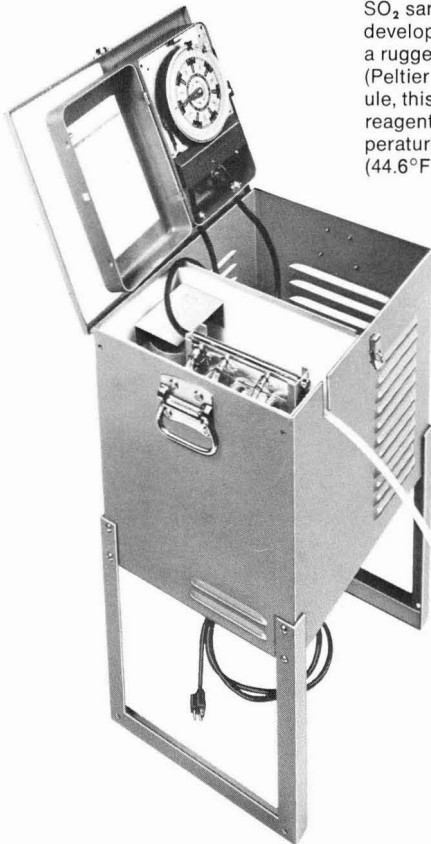
RAC has eliminated this problem in SO₂ sample collection with its newly developed 3-Gas Sampler. Featuring a rugged solid-state thermoelectric (Peltier Effect) cooling-heating module, this instrument maintains the SO₂ reagent (absorbing solution) at temperatures ranging from 7°C to 17°C (44.6°F to 62.6°F).

As a result, all the SO₂ collected during a sampling cycle is preserved for optimum accuracy of sample evaluation. **Another first from RAC!**

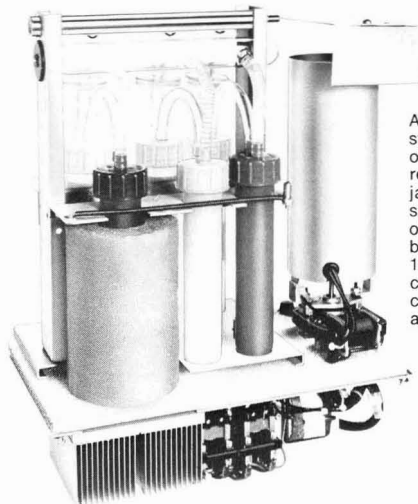
The RAC 3-Gas Sampler is designed to collect nitrogen dioxide (NO₂) and a third (optional) gas simultaneously with SO₂ samples. In fact, it will sample any gas for which there is a suitable reagent, including hydrogen sulfide (H₂S), ammonia (NH₃), and aliphatic aldehydes (CHO).

The latest RAC gas sampler design is available in a portable outdoor model and a smaller, lighter weight indoor model. The outdoor model can be equipped with optional 24-hour or 7-day (skip) timer mechanisms.

For details, send for BULLETIN 2441



Outdoor model of RAC 3-Gas Sampler, with top opened to show installation of an optional 7-day skip timer. An optional 24-hour timer also is available.



A new thermoelectric system controls temp of bubbler with SO₂ reagent (in insulating jacket) for maximum sample stability. Temp of the other two bubblers is kept above 16°C (60.8°F) by enclosed thermostat-controlled heater, at right.

*Modification kit is available to adapt new cooling-heating module to existing RAC 5-Gas Samplers (outdoor models).



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ERT NEWSLETTER

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MEMO

From the desk of the PRESIDENT
To: B. ARRINGTON, ENVIRONMENTAL EDITOR

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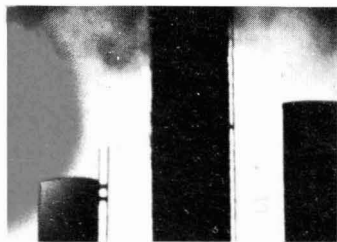
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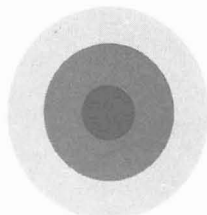
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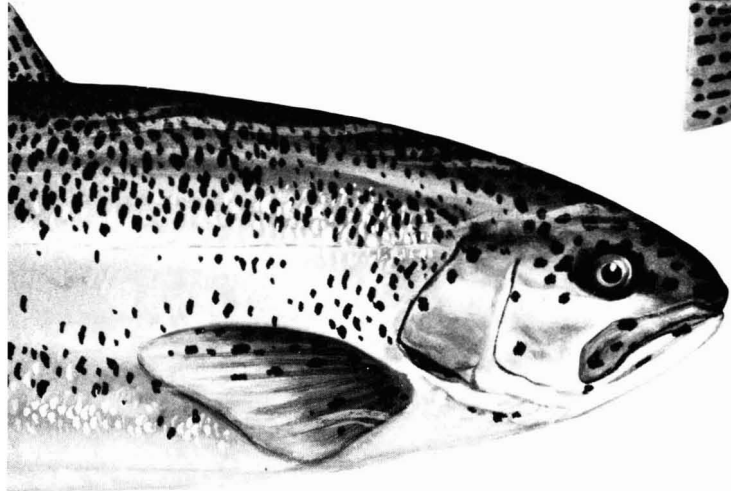
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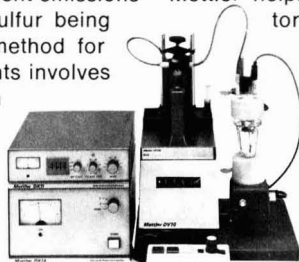
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CIRCLE 12 ON READER SERVICE CARD

Sweet land of liberty

We hear a great deal about individual rights these days and how they are unalterably more important than the rights of the State. Although few U.S. citizens openly oppose this statement, many are deeply disconcerted over the burdensome mechanisms with which governmental institutions implement the principle. The environmental movement like other contemporary social reform efforts is being affected by concern over these mechanisms.

The common perception seems to be that the evolution of a growing list of "rights" has had the curious effect of detracting from our freedoms. The feeling holds that we have more rights than we can count; the right to life, liberty and the pursuit of happiness; the right to live where we choose and work where we are qualified, without racial, sex or religious discrimination; the right to equal pay for equal performance and the right to a healthful environment. Even though the list grows, less freedom is actually perceived by students when applying to competitive professional programs, wage earners when totaling payroll deductions and industrialists and administrators when marketing new materials, siting new facilities or hiring new staff.

Whether or not our rights are innumerable or even excessive is speculative. More certain is the seemingly unavoidable tendency for bureaucratic process to turn well-intentioned guidelines such as affirmative action plans and environmental impact assessments into mindless exercises. Some of the actions designed to protect rights such as requirements for expensive pretesting or extensive study in advance of proposed actions may actually constitute violation of other rights, i.e., the right to be innocent until proven guilty. The result is often confusion, anxiety and, ultimately, institutional paralysis. There may be a social analog to the Uncertainty Principle that forbids the simultaneous possession of personal freedom and an extensive array of individual rights. The rights exist, of course, but concerted efforts to measure, regulate and oth-

erwise secure their existence often seem counterproductive. It was Jefferson who cautioned, "If you give up some freedom for some security you will have neither."

Is there a tradeoff between rights and freedom? Certainly our freedoms have decreased as a result of social and technological advance. One can be "free" through ignorance, and the relative lack of constraints upon our actions in earlier times must be at least partially credited to an unawareness of how our actions affected the well being of others. The essence of the problem, however, is not the relative number of our rights or freedoms. It is liberty. Inefficiency in necessary bureaucratic mechanisms must not be permitted to mask what is really a fundamental exercise in liberty, i.e., the power of freely choosing to constrain those actions that are harmful to others.

The principle is sound as we have freely agreed to voluntarily curtail some freedoms in order to protect more precious ones. The process involves enumeration of rights through legislative actions such as NEPA, Safe Drinking Water Act and the various amendments to the Clean Air and Clean Water Acts. These statements authorize the use of administrative law by selected Federal agencies, which constitutes both what Hardin has called "mutual coercion mutually agreed upon," and a source of irritation when the implementation is handled poorly.

The greatest hazard to our national purpose is not the loss of freedom or unbearable irritation. It is the *unchallenged* overextension of authority by implementing agencies. So long as the testing of agency decisions through social and professional challenges is emphasized, we have preserved what is our most precious heritage—liberty.



ES&T LETTERS

Coal research

Dear Sir: Nominations are solicited for the 1978 Henry H. Storch Award In Coal Research. Administered by the Division of Fuel Chemistry of the American Chemical Society, this Award is given annually to a citizen of the United States who has contributed most to fundamental or engineering research on the chemistry and utilization of coal or related materials in the preceding five years. The award consists of a plaque and an honorarium of \$500. Nomination blanks may be obtained from Dr. G. Alex Mills, Department of Energy, 20 Massachusetts Ave., N.W., Washington, D.C. 20545. Nominations should be submitted by the end of February 1978.

G. Alex Mills

Chairman, Storch Award
Committee of 1978

Impact statements

Dear Sir: In a recent issue, an article (*ES&T*, October 1977, p 952) indicated that past Environmental Impact

Statements (EIS's) could not be found without a "wild agency-to-agency goosechase." Region V of the U.S. Environmental Protection Agency (which includes the States of Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin) has a simple method of locating past EIS's.

We have large, permanent maps of each State, on which pins have been placed to indicate the location of a project that is the subject of an EIS. I conceived of this system in 1971, when our EIS review staff included only two people. It was the only method that could be developed at that time to keep track of all EIS's within Region V without the aid of computers.

The pins are sequentially numbered, and all of the pins used in one year are the same color. Numbers are used to indicate the order in which the draft EIS's were received. Thus, the existence of any past EIS in an area can be determined with a glance. The number and year can be easily found in our project logs, which briefly indicate

each project's full file number, name, the responsible agency, pertinent dates, and EPA's classification of the project and the EIS. When we know the full file number, we can locate the file on any project within minutes. Depending on the project, one can occasionally bypass the log and go directly to the files with a partial project number.

The system has worked well since its inception. Not only can it eliminate a lot of EIS preparation background and baseline duplication, but it can serve to inform other State and Federal agencies of nearby projects that may have environmental effects, some of which can be conflicting. It would be possible to photograph periodically four or five sections of each map in color and publish these exhibits once a year or less with a key to the pin color and number and tabulation of project descriptions in such a form that would be useful to the general public, other State and Federal agencies, environmental organizations, and consulting firms.

Robert L. Kay, Jr.

EPA, Region V
Chicago, Ill. 60604

Trademark

Dear Sir: We wish to refer to the article concerning "Wet Scrubbing of Fly Ash and SO₂" (*ES&T*, November 1977, p 1054).

In the illustration of the Sherco Plant Wet Scrubber System, we note a reference to a Demister® section.

This may or may not be an accurate reference since the word is a registered trademark of our company because of its mesh mist eliminators and entrainment separators. In this illustration, the word is used in a generic sense, and we wish to point out that such use is incorrect.

We are sure you are familiar with the necessity to protect trademarks, and request that if you wish to use the word, it should be given the trademark registration.

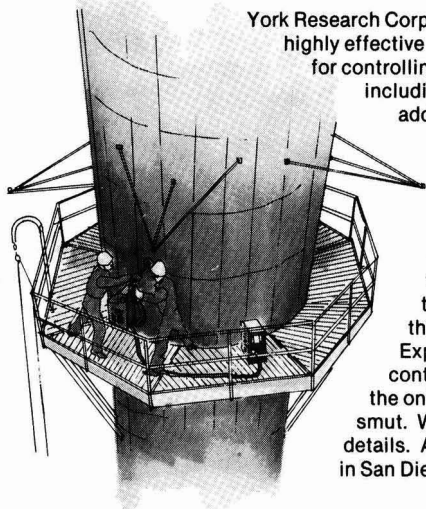
Beyond that, may we say that the article was very interesting and obviously very well prepared.

William D. Matthews,
Vice President
Otto H. York Company, Inc.
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Correction—trillion, not million

In the January 1978 issue it was stated (p 22) that Montana lieutenant governor Ted Schwinden said, "In excess of 1.5 million tons of coal are estimated to lie within the Northern Great Plains Region." The number should have been 1.5 trillion tons of coal.

acid-smut abatement



York Research Corporation has developed highly effective proprietary methods for controlling acid-smut fallout, including the use of fuel-oil additives. Scientists and technicians from three divisions combine skills to ferret out all factors contributing to the problem. They then apply proven techniques to end this corrosive nuisance. Expensive pollution-control hardware is not the only answer to acid-smut. Write for greater details. Ask about what we did in San Diego.



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CIRCLE 9 ON READER SERVICE CARD

INTERNATIONAL

A pilot project to desalt seawater is under way in the Somali Democratic Republic, Hussein Qassim, Minister of Water and Mineral Resources, told *ES&T*. He noted that his country has about 3300 mi of coastline, and that desalted water would be a boon to the generally water-short East African republic. Also, Somalia plans to "make better use of what we have" in the way of water, Minister Qassim said. This effort will involve combatting the schistosomiasis parasite in surface waters (*ES&T*, Sept. 1977, p 848), and expanding groundwater supplies, especially for agriculture, in the 600 000-km² nation. At present, about 200 wells/year are being drilled, but Minister Qassim hopes to see a material increase in that number in the very near future.

WASHINGTON

P.L. 95-217, the 1977 amendments to the Federal Water Pollution Control Act of 1972 was signed into law by President Jimmy Carter. Among its nearly 80 provisions, the act authorizes \$28.7 billion for clean-up measures, \$24.5 billion of this amount going toward municipal waste treatment plant matching grants. The 1983 deadline for best available technology (BAT) was pushed back to July 1, 1984, and the EPA would have to apply a test of "reasonableness" before it strengthened effluent standards for industry that has already met the 1977 best practicable technology standard. Three classes of pollutants were set up: conventional pollutants (BOD, TOD); nonconventional pollutants (metals, organic nitrogen); and toxic pollutants. Some 139 substances are listed in the latter category, and these and other compounds that are added later are subject to BAT control, at a minimum.

EPA has issued new rules ordering chemical companies to report every product they made in 1977 to the agency by May 1. These were the

first rules issued under the 1976 Toxic Substances Control Act. It is estimated that these rules will affect 5400 domestic chemical producers and petroleum refiners that produce 50 000-70 000 chemicals. Producers with sales exceeding \$5 million must also report the quantity of the chemical manufactured and where it is produced. Steven Jellinek, EPA's assistant administrator for toxic substances said that



EPA's Jellinek

the new rules would permit the agency to review and rule on all new chemicals (about 1000/y) introduced to the marketplace after 1977, and would be "a powerful incentive to the chemical companies to produce chemicals that are safer."

The EPA reports that air quality is improving, although parts of the U.S. still experience severe smog problems. The agency's *National Air Quality and Emission Trends Report for 1976* shows that from 1970-1976 sulfur dioxide levels decreased by 27%, carbon monoxide levels dropped 20% and smoke and dust decreased by 12%. However, smog, particulate matter and nitrogen dioxide all increased from 1975 to 1976. The report states that smog "ranks today as one of the most serious and pervasive air pollution problems in this country." Drought during 1976 was one explanation for the increase in particulates. Nitrogen dioxide increases were attributed to motor vehicles and power plants, but the report cautions that insufficient historical

data prevent definitive conclusions to be drawn.

TVA is the worst polluter per unit of electricity generated among 15 large utilities studied by the Council on Economic Priorities (CEP). The best pollution control record: Pacific Gas and Electric (San Francisco, Calif.). The CEP study found that "overall control of the three air pollutants (particulates, sulfur dioxide and nitrogen oxides) has shown only slight improvement at best," but thermal discharges have been substantially reduced. CEP concludes that increases in coal usage to generate electricity have canceled improvements in pollution abatement in the electric utility industry. TVA, the nation's largest electric utility, ranked at the bottom for both air and water pollution control. CEP felt that the reason for this was TVA's use of high-sulfur coal and "its resistance to the use of state-of-the-art pollution control equipment."

The Dept. of Labor reports a 13% decrease in job-related deaths from 1975 to 1976, but a 3% rise in job-related injury or illness. Because of a proportionate rise in hours worked, the incidence rate at 9.2 injuries and illnesses/100 full-time workers remains unchanged from 1975. The survey was compiled by the Bureau of Labor Statistics from reports submitted to the department during 1977 by employers in the private sector.

CEQ and DOE are underwriting a project to develop ways of mediating energy-environment disputes. The American Arbitration Association will conduct a 6-month study to identify five disputes and delineate the steps of mediation needed to resolve them. After this first phase, the actual resolution of some or all of the five cases will probably be pursued.

The SBA proposed rules for pollution control financing guarantees. The rules apply to the purchase of air pollution, water pollution and

noise pollution control facilities, and are designed to implement amendments to the Small Business Act and the Small Business Investment Act passed in 1976. The Small Business Administration conducted a pilot program in California (*ES&T*, April 1977, p 329).

STATES

TACB was denied a waiver of Clean Air Act emissions offset requirements by the EPA. The Texas Air Control Board had petitioned the EPA for a waiver on September 22, and supplied additional information on this petition on November 8. The request was made under Section 129 of the Air Act Amendments of 1977, which allows a state to administer its own growth policy if EPA determines that the state's program provides for reductions in emissions sufficient to assure attainment of national ambient air quality standards by 1982. EPA in denying the waiver said that "Based on our review of the material . . . the Texas program would require modification in several major respects before a waiver could be granted."

Minnesota's Pollution Control Agency (MPCA) is developing a plan to control urban runoff. Specifically, MPCA's Water Quality Management Plan will control, prevent or abate pollution from stormwater runoff and other non-point sources. The Twin Cities Seven-County Metropolitan Council will assess the severity of an urban runoff problem in the Twin Cities Metropolitan Area, and MPCA will assess the problem and offer management programs for controlling or preventing problems outside the Twin Cities Seven-County Metropolitan Area. MPCA will examine runoff in Morris, Thief River Falls, Gilbert and Stewartville. These cities were selected for their land-use characteristics, geographic location, and population and density variations. Programs will be developed to control or prevent urban runoff.

Illinois Governor James R. Thompson urged a national policy on the handling of nuclear wastes. Thompson, in a letter to Rep. Leo Ryan (D, Calif.), chairman of the House Environmental Energy and National Resources Subcommittee, said that "The production, transportation, storage and disposal of

hazardous and nuclear wastes is an issue with overriding national dimensions. But the response of the federal government to this challenge is a sorry one." Illinois has provided a favorable climate for industries using nuclear material, but



Ill. governor Thompson

Thompson remarked that "Illinois' willingness to cooperate in this area threatens to make the state the dumping ground for the nation," because of the "failure of the federal government to develop a national policy on the use and disposal of nuclear material."

Air monitoring data from California's Bay Area indicate that 1977 was the cleanest year on record. There was a continuation in the downward trend in oxidant levels and there were no days exceeding the 0.20 ppm oxidant level necessary for a smog advisory/alert. The federal oxidant standard of 0.08 ppm was exceeded 41 days throughout the Bay Area in 1977, 64 days in 1976 and 69 days in 1975. San Francisco, Richmond, Oakland, Santa Rosa, Petaluma, Burlingame and Pacifica monitoring stations showed no excesses of the oxidant standard in 1977, and only Livermore, Alum Rock and Los Gatos stations had 15 or more days over the standard. Los Gatos was the only station to show an increase last year.

Twenty-three states now have laws or resolutions encouraging the adoption of solar energy systems according to the latest National Bureau of Standards survey, "State Solar Energy Legislation of 1976: A Review of Statutes Relating to Buildings." According to this survey, 44 bills out of 150 proposals were adopted by state legislatures. In 1975, 120 bills were introduced among the states, and 20 bills were passed. Last year, 9 states took measures to provide tax incentives for the installation of solar energy devices. And three states approved

laws supplementing those passed in 1974 or 1975. The 12 states providing financial incentives were Ariz., Calif., Conn., Ga., Hawaii, Idaho, Kans., Md., Mass., Mich., Vt. and Va. To date, 17 states provide tax incentives.

MONITORING

The results of the Biological Monitoring Inventory project begun in 1975 and sponsored by CEQ, the Dept. of Energy, the National Marine Fisheries Service and the U.S. Fish and Wildlife Service, have been compiled in a report entitled, "National Inventory of Selected Biological Monitoring Programs." The report (ORNL/TM-5792), published by environmental scientists at Oak Ridge National Laboratory (ORNL), can be obtained from the National Technical Information Service. This inventory was the first effort to identify and classify biomonitoring projects in the U.S. The survey revealed that more than \$150 million is now being spent each year on biological monitoring activities, but duplication and gaps remain. Inventory information is computerized and available through DOE/RECON or ORLOOK, an ORNL information-retrieval system.

Air quality and meteorological conditions will be monitored along 3 segments of the Wisconsin and Mississippi Rivers to find best sites for Wisconsin Power & Light Co.'s coal-fired power plants (each 300 MW). Dames & Moore (Los Angeles, Calif.) will install and operate monitoring stations.

Ozone (O₃) in ambient air can now be monitored by the chemiluminescent reaction of O₃, and rhodamine-B. Previously unreliable, the method is now valid when rhodamine-B and gallic acid are used in a sintered-glass disc. N.V. Philips' Gloeilampenfabrieken (Holland) developed the technique.

TECHNOLOGY

More than 20 public water supply wells had to close because of pollution by industrial wastes, suspected carcinogens, and toxic heavy metals, Olin Braids of Geraghty and Miller, Inc. (Port Washington, N.Y.) told an ACS meeting at Little Rock, Ark. Contaminants reached depths of 125 m in aquifers, Braids noted.

Reduction of phosphorus in wastewater to less than 1 ppm is the object of installing Union Carbide's PHOSTRIP system at the Erie County-Southtowns Sewage Treatment Agency (N.Y.). The system uses a combination of biological and chemical treatments to cut phosphorus concentration, and, in this case, will work in a 16-mgd facility. Union Carbide engineered the system under license from Biospherics Inc. (Rockville, Md.). It is expected that use of PHOSTRIP will bring about savings of \$60 000/y over "conventional" chemical precipitation methods.

Solar heat storage becomes practical and cost-effective by use of sodium sulfate (Na_2SO_4), which has at least 7 times the storage ability of an equal amount of water, and 12 times that of rock, General Electric says. The trick is a cylinder, rotating at 3 rpm, in which the Na_2SO_4 is loaded. Rotation obviates problems of poor salt freeze-thaw and heat transfer.

How might you treat wastewater in one-third of the area normally needed? Try the ICI Deep Shaft Effluent Treatment System, such as that being installed at Virden, Man., Canada, for \$2 million. It will handle 500 000 imp/gpd, which is sent underground 500 ft and sealed from surrounding subsurface territory. Compressed air furnishes oxygen necessary for biological oxidation, as well as the force necessary for circulating liquid effluent in the shaft. Treated effluent is then disinfected prior to discharge to the Assiniboine River. Developed by Imperial Chemical Industries Ltd. (Britain), the system is marketed in Canada by Eco-Research Ltd. (Calgary, Alta.).

Does reduction of NO_x emissions always decrease O_3 in smog? Not always, according to General Motors. In fact, a GM study indicates that in some cases, NO_x reduction may actually accelerate O_3 formation, according to results of a study in the Los Angeles area. Smog chamber simulation tests showed that at nearby Riverside, for instance, a 0.5-ppm NO_x level, after 12 hours of solar irradiation, could lead to an O_3 level near 0.2 ppm. But an NO_x level of 0.3 ppm could, under the same conditions, cause the O_3 level to be near 0.3 ppm. Similar results were found for urban Los Angeles, according to GM Research Laboratories.

Suppression of emissions from many different materials tested for combustibility and smoke generation is done in tandem with a cooling tower at Factory Mutual System (West Gloucester, R.I.). Several of the system's components use a corrosion-resistant new technology involving balsa and fiberglass-reinforced plastic (FRP). Owens-Corning Fiberglas supplied the FRP. Smoke ducts are linked to the cooling tower; smoke is cooled to about 100 °F, and is "doused" with 1000 gpm of water. Venturi scrubbers, electrostatic precipitators, cyclone collectors, exhaust fans, and stacks are among the components of the 100 000-cfm smoke removal system.

INDUSTRY

Proposed federal taxes on certain packaging materials are "ineffective, regressive, discriminatory, and inflationary," and wouldn't solve the nation's garbage disposal problems, Judd Alexander, senior vice president of American Can Co.,

said. "The taxes would probably pass anyway," he predicted. Alexander said that state taxes would be just as disruptive and ineffective as federal taxes. He estimated that costs of beverages, for instance, would rise by some \$1.2 billion/y if



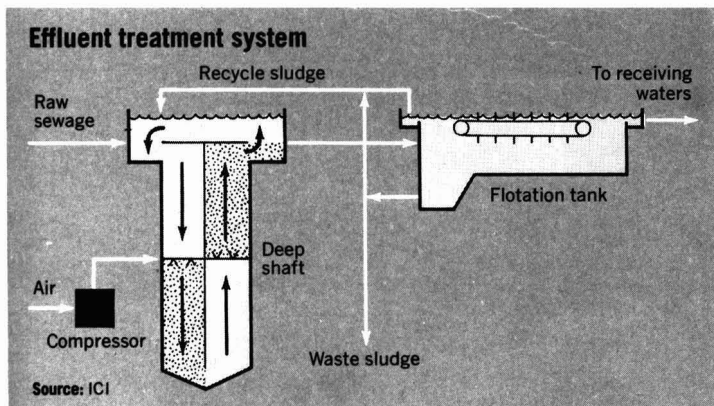
American Can's Alexander

proposed deposit legislation takes effect, whereas if all cans and bottles were eliminated from the waste stream—a practical impossibility—garbage collection savings would be only \$120 million.

Homes with solar-assisted heating/cooling, including 600 floor plans, and able to save up to 60% of energy costs in a northern climate, are available from National Homes Corp. (Lafayette, Ind.). National and Dow provide unique insulation packages; hot water is furnished by a Revere Corp. solar energy system; and heating/cooling is done with a GE heat pump. National says that these homes are "affordable." Also, the Bank of America is opening its first "solarized" branch at Palm Desert, Calif., and has announced availability of financing for solar energy as part of its home improvement loan package program.

Ford Motor Co. has a "revolutionary" dust collection system installed at its huge Rouge manufacturing complex at Dearborn, Mich. The system is mainly a 14-compartment baghouse, and captures fumes during melting down, charging, slagging, and tapping in a 123 500-ft² furnace shop. Ford says that the zero-emissions target is being rapidly approached.

Peabody International Corp. is supplying the first hydrogen peroxide odor-control scrubber to the Ocean County Sewer Authority (Bricktown, N.J.). The idea is to react hydrogen sulfide after it is absorbed by a caustic solution. Water and elemental sulfur are produced.



There are problems, but there's enough promise to justify plans for large demonstration plants that will be important milestones for

Fluidized-bed combustion's progress

An interesting, though unfortunate historical phenomenon is that certain technologies, which could be both scientifically and economically feasible, somehow get lost in the shuffle. An example is fluidized-bed combustion (FBC) technology which, in fact, has been known for about 100 years. However, it was not the object of much serious work until the 1960's. Thus, as Valeryy A. Ovrachenko (U.S.S.R.) of the United Nations Center for Natural Resources, Energy, and Transport, observed, the conference he was addressing might have been the fiftieth.

But because of the relatively recent time in which FBC began to receive serious consideration, what Ovrachenko addressed was the Fifth International Conference on Fluidized Bed Combustion, held in Washington, D.C., in mid-December. It attracted some 500 attendees from the U.S., and foreign countries, and was convened by the METREK Division of the MITRE Corp. (McLean, Va.), the U.S. Department of Energy (DOE), EPA, and the Electric Power Research Institute (EPRI, Palo Alto, Calif.).

"Out on a limb"

"I am ashamed that TVA is the biggest air polluter in its area, but I hope that we won't be one much longer," S. David Freeman of that power system's board of directors declared in his keynote address. "We must design new technology that will exceed regulations," he added.

Thus, TVA and DOE let a contract to Foster Wheeler Energy Corp. (FWEC), via Stone & Webster Engineering Corp., to design and "cost out" commercial application of atmospheric FBC (AFBC) steam generators. The idea is to compare design/costs of a 570-MW AFBC unit with those of a

similar-sized pulverized coal (PC) fixed-bed unit with scrubbers. Another contract, to let to FWEC through Fluidized Combustion Corp., aims at a 150-MW demonstration-size AFBC unit. Scale-up to 600 MW is envisioned.

Freeman said that TVA "is going ahead, out on a limb, even," with plans for a 200-MW demonstration pressurized FBC (PFBC) system. He also



TVA's Freeman
taking some calculated risks

noted that FBC, whether atmospheric or pressurized, "fits into TVA's plans to innovate." Freeman hopes for some type of FBC scale-up by 1983. But he posed some questions; one of great significance concerned the ability of FBC to handle small particulates. "If it can't, then it is not an advance," he said.

Nevertheless, Freeman expressed hopes for FBC's future. He noted that

the U.S. must use coal "to turn loose from oil slavery." TVA helps to meet that goal by being the largest coal purchaser in the U.S., Freeman observed. He also said that further energy and pollution objectives will be met through electrification of the transportation sector.

Cautious optimism

Public Law 93-577, the Federal Non-Nuclear Energy Research and Development Act of 1974, calls for a joint government/private sector effort to develop environmentally "clean" demonstration ("demo") plants. One of the main thrusts of this development concerns scale-up and evaluation of AFBC. This would be in harmony with a national goal of having all fossil-fueled power generation converted to coal by 1990, as per the evolving National Energy Act, DOE's Edward Trexler told the conference. Included in the "demo" plants evaluation program are to be planning, conceptual design, technology, and marketing.

But new source performance standards (NSPS) could be a problem for FBC units. Trexler explained that these standards are "tough and unstationary," and changing standards make technological and investment planning and activity very difficult. Present NSPS for SO₂ are 1.2 lb/10⁶ Btu, for example, but they could go as low as 0.2 lb—that is, 90% capture to a low limit of 0.2 lb, with 1.2 lb maximum for a given time interval. NO_x might be lowered from 0.7 to 0.6 lb/10⁶ Btu. Particulates—which FBC *per se* does not abate—may have standards lowered from 0.1 to 0.03 lb/10⁶ Btu.

Nevertheless, Trexler is "cautiously optimistic" that FBC will prove to be able to comply with such standards. He said that designs must make use of

the data base compiled, in order to lead to smaller, more efficient FBC systems with better sorbent (limestone, for example) use.

Development teams

Before FBC can truly reach the "demo" stage, certain essential design information must be obtained. Accordingly, DOE is sponsoring a program for a nominal 600-MW utility AFBC steam generating plant to obtain this sort of design information. Three designs are under development by

- a Burns and Roe/Combustion Engineering design team
- a Stone & Webster/Foster Wheeler Energy Corp., design team
- a Stone & Webster/Babcock & Wilcox design team

Radian Corp. (McLean, Va.) was retained by DOE to provide technical assistance and support in the form of information reviews, and to compare and assess how each design team proposes to handle specific problems associated with AFBC operation.

A Radian spokesman pinpointed three such problems at the outset. Two are technical, and one is environmental. One technical problem concerns calcium sorbent utilization; its purchase, its calcining, and efficient use and disposal of spent sorbent. The second technical problem involves the finalization and optimization of AFBC controls for which the engineering picture still requires a certain amount of clarification.

Fly in the ointment

A real "fly in the ointment", however, can be changing environmental standards. Designing an AFBC, or, for that matter, a PFBC system can be

exceedingly difficult if, say, SO₂ standards present a moving target.

What helps to complicate things is the operation of the carbon burn-up cell (CBC), a component that may come downstream in a system from the utility AFBC combustor itself. Now the main AFBC combustor cells may capture 90% of the coal's sulfur, for example, but actually retain only 80%. However, future NSPS may—probably will—require 90% SO₂ capture. If that requirement is indeed established, the CBC could pose some technical problems because it would have to operate at the same lower temperature as the main FBC cells in order to capture SO₂. Normally, a main FBC cell might function at about 1500 °F, whereas a CBC should work at about 2000 °F, if its performance is not to suffer.

Another difficulty that very stringent SO₂ standards could raise is the need for high calcium-to-sulfur (Ca/S) feed ratios. Higher Ca/S ratios would, in turn, lead to an increase in solids handling/disposal facility needs, according to Radian. Moreover, increases in sorbent needs could bring about losses in sensible and latent heat to the extent that boiler efficiency would be driven below acceptable levels.

In foreign lands . . .

Meanwhile, in England, work continues on PFBC. H. Raymond Hoy of BCURA (*ES&T*, February 1976, p 121) told the conference that the effort now concerns a 3 ft by 2 ft pressurized combustor at the National Coal Board's research facility at Leatherhead. Fluidizing is at 7 ft/s; beds are 8 ft deep, and a 7-ft-tall tube tank is provided. What Hoy and his associates

found was that combustion efficiency, SO₂ retention, and elutriation were "satisfactory," but that 2.5 ft/s is probably a better fluidization velocity for these three variables.

Another effort in England, at the University of Aston in Birmingham, touches on rotating FBC combustors. That university's J. Howard said that these rotating combustors offer "exciting prospects" of raising the rate of heat release per unit volume of bed to "dramatically high levels." But Howard cautioned that this type of system is very much in its infancy, and that certain problems—for instance, in start-up and control—must be overcome.

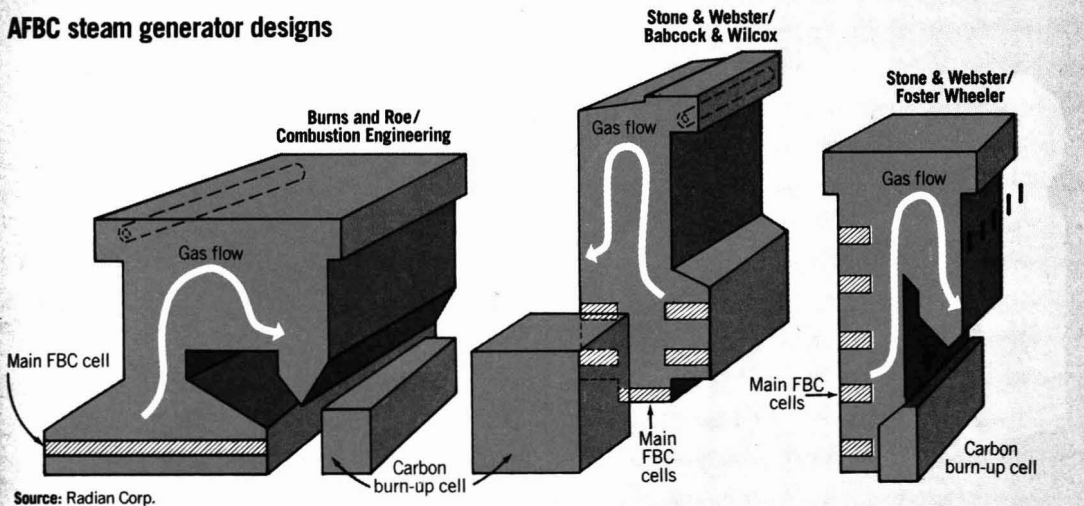
NO_x problems were not ignored. In Japan, where NO_x is of particular concern, the University of Nagoya is evolving a basic concept for a low-NO_x FBC system. And Hiroshi Terada of Babcock Hitachi Co. (Hiroshima) noted that results of work by his company with a 3.4-ft² FBC pilot plant indicate that NO_x could be controlled to meet Japan's very stringent standards by means of "reasonable" two-stage combustion.

NO_x work is also on-going in the U.S. Janos Beér and his colleagues at Massachusetts Institute of Technology found that NO can be reacted with char under controlled feed, particle size, and temperature conditions to achieve as much as 100% conversion to CO, CO₂, and nitrogen.

Not sanguine, but hopeful

One recent evaluation of FBC—at least, AFBC—was that it is a proven technology, ready for commercial scale-up (*ES&T*, November 1977, p 1048). The general consensus at the conference seemed not to be quite as

AFBC steam generator designs



Source: Radian Corp.

sanguine, although all certainly agreed that a great promise is there, and that FBC has come an amazingly long way.

But there is yet quite a way to go. Controls and sorbent use (Ca/S ratios, and the like) must be optimized, for

example. CBC problems must be solved. So must those of NO_x and particulates; all in such a way that boiler efficiency is not impaired. One can list other difficulties.

However, these difficulties appear to be those of engineering, and do not

seem to compromise any of the basic soundness of FBC principles. So one can be quite hopeful that FBC could indeed become one of the viable options for expanding the nation's use of coal without undue deterioration of its air resources. JJ

Permanent and safe disposal of toxic and hazardous materials may require

The "fire" next time

When America was younger, money freer and environmental restrictions more lax, industries could afford to burn their liquid wastes. Sixty years ago waste oils were being burned. And Dow Chemical Co. in Midland, Mich., reportedly has been burning its by-product organic wastes for decades.

Today's economic and environmental climate dictates that toxic and hazardous wastes be disposed of safely and permanently, or gleaned for their material resources or energy. The only sound environmental disposal treatment may be incineration with energy and resource recovery.

With the passage of the Toxic Substances Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA) last year, not to mention the lack of available land, landfilling of liquid toxic and hazardous wastes is becoming a less acceptable disposal alternative. But the incinerators of yore—essentially burners with an oxygen source—that could thermally destroy combustible hydrocarbon

wastes are not the technological solution to today's disposal problems.

Today's incinerators are sophisticated, highly engineered "tin-lizzies" custom-designed to meet specific disposal problems.

Why this article?

Empirically it seemed apparent that the plethora of federal pollution control laws, especially TSCA and RCRA, would force industries with toxic or hazardous liquid waste to turn to incineration as a viable disposal alternative. To test this assumption, *ES&T* sent a questionnaire to those companies that listed their business as liquid waste incinerators in *ES&T's* October 1977 "Pollution Control Issue."

Slightly more than 25% of those companies receiving questionnaires answered them. However, the information they supplied was sketchy at best, but subsequent telephone interviews fleshed out their responses a bit. The National Solid Wastes Associa-

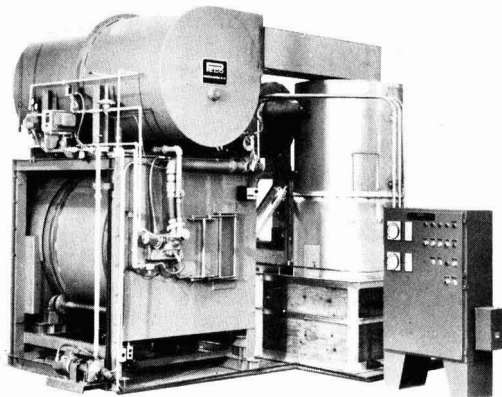
tion (Washington, D.C.) and the Combustion Institute (Pittsburgh, Pa.) were also contacted, but they could not furnish substantive information.

One company, which in lieu of completing the questionnaire sent a slick noninformative brochure, told *ES&T* that the questionnaire was a marketing survey that would cost the company \$5000 to complete. Nevertheless, several companies did complete the questionnaire, and the following points became evident:

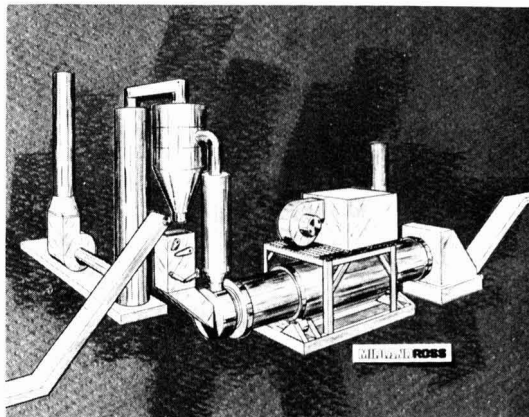
- No market survey of the liquid incineration industry has been published.
- No two incinerators are alike. Companies that build incinerators for the disposal of liquid wastes custom-design their units to the specific disposal needs of their customers.
- Companies building these incinerators often do not know their competition, or have incomplete knowledge of their competitors.
- No trade association representing this industry exists, although the American Incineration Institute did exist until 1975 when the general market downturn forced most of its members out of business.
- Companies actively building and selling these units expect the legislative climate to act as a market stimulus.

A generalized description

A complete incineration system usually consists of a waste-feed system



Progressive Equipment's liquid waste incinerator



Midland-Ross' toxic/hazardous liquid disposal system

that delivers the liquids, slurries, sludges and even solids to the thermal destruction chambers—generally separate oxidation and gasification chambers. If in the process of destroying the wastes, particulate matter is formed, the incinerators can be equipped with venturi scrubbers or baghouses to control airborne emissions; a waste heat recovery unit can also be included in the system.

These units operate at temperature regimes of about 1000 °F (and as high as 2400 °F), and with residence times that vary between 1 to 3+ s. The liquid handling capacities of the units described to *ES&T* range from 20–300 gph.

The units may be of standard design, but are more likely to be custom-engineered. State and federal operating permits are required.

A market sketch

To paint a picture of the market for these incinerators, *ES&T* asked the companies to describe their markets in terms of sales, targeted industries/municipalities and growth projections. Because of the sketchy answers received, the financial picture could only be painted in broad strokes.

The prime targets for this type of disposal equipment are the chemical process industry; the petrochemical industry; industries producing sludges and/or slurries that contain toxic or hazardous components; municipal sewage treatment facilities; and federal government facilities.

Several companies reported that they have already experienced their maximum growth rates, and sales have leveled off between \$1–3 million (for liquid waste incinerators only). The reasons given for this stable condition were a marketing strategy whose thrust is now in solids and sludge rather than liquid waste incinerators, or nearly complete penetration of a geographically well-defined market.

One company, which acquired a liquid incineration system from another firm only one and a half years ago, expects its growth potential to be very good in the future. While still another company expects its sales to increase by 214% in fiscal 1978 over last year's sales.

Claiming not to know the financial status of the incinerator manufacturing industry, no company would, with certitude, claim its share of this market. One company gingerly ventured that it might have 10–15% of the total market, while another claimed to have 70% of the market in its precisely defined geographic area.

So diffuse is this industry that there

is no agreement on the top five to ten companies building liquid waste incineration equipment. However, the companies cited more than once were CEA Combustion, Copeland Systems, Midland-Ross Surface Division and Trane Thermal, in alphabetical order.

Basically the companies saw no technological breakthroughs in the near future. They did, however, speak of novel applications of thermal processing methods or novel combinations

Companies building liquid waste incinerators

Ametek Process Systems
Babcock & Wilcox
Bayco Industries of Calif.^a
W. N. Best Combustion
Equipment
CEA Combustion
Copeland Systems
Envirotech^b
Matthey Bishop
Met-Pro Systems^a
Midland-Ross Surface Division^a
North American Manufacturing
Progressive Equipment^a
Reeco
Trane Thermal
Trecan
Union Carbide
Vulcan Iron Works
Wheelabrator-Frye
Zimpro (wet-air oxidation)^a

^a Answered questionnaire

^b Experience in the area limited

of existing technology to properly dispose of noxious wastes and concomitantly recover valuable and scarce resources and energy.

Succinctly, most companies envisioned "high-levels of refinement," rather than technological innovation in the next five years. They cautioned that waste generators from now on would have to study, in the words of David Schoen of Midland-Ross Surface Division, "all disposal procedures . . . carefully . . . as to ecological soundness and economic return."

The method of choice

Ecological soundness and economic return. If these remain the watchwords for industry, then as Met-Pro Systems Division points out, with "landfills closing and [waste] hauling and disposal costs skyrocketing," incineration

may, of economic necessity, become the disposal method of choice. Bayco Industries of California confirms this assessment, but adds that an "increased emphasis on thermal recovery . . . may make this equipment more economically feasible."

Since incineration is capable of reducing environmentally problematic substances to their basic elements or to innocuous compounds, permanent and ecologically safe disposal of these toxic or hazardous materials becomes possible. As long as modern chemical/technological ingenuity is fostered, the potential for producing noxious waste is encouraged. Incineration then "will remain the only viable form (of disposal) within the next 20 years," according to Mitch Gorski, Jr., of Progressive Equipment Co.

Experimental "burns" of highly toxic materials have been conducted successfully. Midland-Ross ran test burns on the pesticide Kepone in its pilot test facilities at Toledo, Ohio. Using the temperature regimes and residence times worked out by scientists at the University of Dayton Research Institute, Midland-Ross "developed the technological feasibility of thermal decontamination of residues at about 1000 °F and destruction of the compound vapors (99.999% or greater) at 1900 °F and above."

A Canadian "burn"

Recently the Belgium publication *Ecochem* described an experimental program at the St. Lawrence Cement Co., a Canadian firm. Test burns of mixtures of ethylene dichloride, chlorotoluene and polychlorinated biphenyls demonstrated that the materials could be destroyed with a 99+ efficiency without polluting the atmosphere. And, because chlorinated hydrocarbons with about 40% chlorine were incinerated, oil consumption for the kiln was decreased.

In this experiment, organic wastes were converted to assets. In cement kilns, these wastes were able to replace other forms of chlorine used for the reduction of alkali content. Incineration of these wastes converted formerly persistent and toxic pollutants to harmless compounds, and at the same time recovered useful heat values. In this experiment, economic savings, energy recovery and an environmentally safe disposal method were realized.

Outlook: optimistic

It soon becomes evident that the companies that answered the questionnaire are not simply selling incinerators. On the contrary, they are

selling their expertise for innovative design to solve the most difficult disposal problems.

It is clear that this segment of industry—the builders of incineration equipment—does not see the new Clean Air Act Amendments, the new Water Control Act Amendments, the

Toxic Substances Control Act and the Resource Conservation and Recovery Act as constraints to future growth. In contrast to the rest of industry, quite the opposite is true.

These companies see liquid waste incineration as an economical and ecologically sound solution to the dis-

posal of "contaminated and sensitive materials." As the federal laws place environmental constraints on industry as a whole to properly handle and dispose of its wastes and, to the extent possible, recover valuable materials and energy, the business of liquid waste incinerators will grow. LRE

Environmental program

Come to Cleveland for the 29th Pittsburgh Conference. You will see a display of instrumentation from 340 companies. You will hear the following program. We will see you there. The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Cleveland Convention Center Feb. 28–Mar. 3

February 1978

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Wednesday, March 1 Environmental Analysis—General I

Wednesday Morning, Music Hall
J. O. Frohlinger, Presiding
University of Pittsburgh

8:30 (367) **Carbon partitioning of an Aquatic Ecosystem by using an Organic Carbon Analyzer**—*J. C. Perkins, P. E. Edmunds, Duke Power Company*

8:50 (368) **Diffusion Tubes as a primary standard for OSHA Type**

Calibration—*F. J. Debbrecht, D. T. Daugherty, E. M. Neel, Analytical Instrument Development*

9:10 (369) **Differential Thermal Analysis (DTA) with a Minicomputer Programming and Data Handling**—*O. Menis, National Bureau of Standards, J. A. Mackey, P. C. Ruegg, J. F. Barkley, P. D. Garn*

9:30 (370) **Automatic Analyzer for traces of dispersed oils in waste water by Solvent Extraction-Infrared Spectrophotometry**—*N. Yamaguchi, R. Suzuki, R. Matsumoto, Fundamental Research Laboratories of Nippon Steel Corporation*

9:50 (371) **Automated determinations of Sulfur in Fossil Fuels**—*D. Gibboney, Fisher Scientific Company*

10:10 **Recess**

10:20 (372) **An improved design for the analysis of Microliter Samples by Fluorescence and Room Temperature Phosphorescence**—*G. Walden, J. Bradshaw, J. D. Winefordner, University of Florida*

10:40 (373) **The analytical performance of Room Temperature Phosphorimetry**—*E. L. Yen, J. D. Winefordner, University of Florida*

11:00 (374) **Application of the Microwave Plasma Detector to problems in Environmental Pollution**—*J. S. Hobbs, Applied Chromatography Systems, Ltd.*

11:20 (375) **An investigation of error in the Low-Range Chemical Oxygen Demand Determination**—*L. L. Stookey, B. A. Klein, Manchester Laboratories*

11:40 (376) **Total Carbon, Total Organic Carbon and Carbonate Carbon determinations in water and various solid materials using a Coulometrics Carbon Analyzer**—*E. W. D. Huffman, Jr., Huffman Laboratories*

Wednesday, March 1 Environmental Analysis—Organic

Wednesday Afternoon, Music Hall
R. M. Raybeck, Presiding
Jones & Laughlin Steel Corporation

1:30 (441) **Concentration and analysis of Organic Compounds from air and water**—*W. Averill, J. E. Purcell, Perkin-Elmer*

1:50 (442) **Determination of Trace Organic Impurities in water using Thermal Desorption from XAD Resin**—*J. S. Fritz, J. Ryan, Iowa State University*

2:10 (443) **Analysis of Carginogenic Gases in Ambient Urban Air**—*B. Kibbekus, J. Bozzelli, New Jersey Institute of Technology*

2:30 (444) **Trace organic compounds in water by Liquid Chromatography**—*H. F. Walton*, G. A. Eice-man, University of Colorado

2:50 (445) **Concentration and/or separation of Organics in Eco-Systems by Functional Group Specific Polymer Resins**—*T. J. Mourey*, R. Kostyla, S. Siggia, University of Massachusetts

3:10 **Recess**

3:20 (446) **Comparison of two techniques for the collection and analysis of Polynuclear Aromatics in Ambient Air**—*J. L. Lindgren*, Texas Air Control Board, H. J. Krauss, M. A. Fox

3:40 (447) **Collection and quantitative analysis of some C₁-C₁₂ Hydrocarbons in Texas Urban Air**—*J. L. Lindgren*, Texas Air Control Board

4:00 (448) **The determination of Volatile N-Dialkylnitrosamines in Ambient Air**—*J. A. Cucco*, P. R. Brown, University of Rhode Island

4:20 (449) **New Column Technology in the analysis of Organics in water by Gas Chromatography**—*R. Mindrup*, Supelco

4:40 (450) **Monitoring of Fresh-water Organic**—*J. A. Pattison*, Digicolor, Inc., G. Amey

Thursday, March 2

SYMPOSIUM

Airborne Contaminants

arranged by

R. W. Freedman,
U.S. Bureau of Mines

Thursday Morning, Room 235A

R. W. Freedman, Presiding

8:30 (487) **Continuing Problems in sampling and Chemical Speciation of Sulfate in Airborne Particles**—*R. L. Tanner*, Brookhaven National Laboratories

9:10 (488) **Critique of procedures for Nitrogen Oxides**—*B. Saltzman*, University of Cincinnati

9:50 **Recess**

10:00 (489) **Analysis of Human Carcinogens in Polluted Atmospheres**—*E. Sawicki*, National Environmental Research Center

10:40 (490) **Various difficulties associated with field sampling of Airborne Particulates**—*M. Corn*, N. A. Esmen, University of Pittsburgh

11:20 (491) **Polynuclear Aromatic Hydrocarbons in Environmental Samples—their characterization by an**

X-ray Excited Optical Luminescence Technique—*V. A. Fassel*, C. S. Woo, A. P. D'Silva, Iowa State University

Thursday, March 2

Environmental Analysis—General II

Thursday Afternoon, Room 235A

J. P. Auses, Presiding

Alcoa Laboratories

1:30 (571) **Computation of error estimates in Total Elemental Content Passive Dosimeters**—*J. G. Montalvo, Jr.*, Gulf South Research Institute

1:50 (572) **Improved Data Processing Software for Glass Capillary Separations of Complex Environmental Samples**—*E. B. Overton*, C. F. Steele, J. L. Laseter, University of New Orleans

2:10 (573) **Field Measurements of Atmospheric Methane with a two-wavelength Laser System**—*C. F. Dewey, Jr.*, Massachusetts Institute of Technology

2:30 (574) **Application of Glass Open Tubular Gas Chromatography to Environmental Samples**—*S. C. Madden*, W. L. Winterlin, J. N. Seiber, T. J. Mast, University of California

2:50 (575) **Collection and determination of Trace Amounts of Organo-Thiophosphates in air using XAD-2 Resin**—*F. Kaminski*, R. G. Melcher, Dow Chemical U.S.A.

3:10 **Recess**

3:20 (576) **The determination of Nickel Carbonyl**—*J. E. Campana*, T. H. Risby, Pennsylvania State University

3:40 (577) **Collection, separation and analysis of Organic Vapors by Computerized GC/IR**—*D. Goldfarb*, C. W. Brown, University of Rhode Island

4:00 (578) **In Situ determination of Total Particulate and Dissolved Organic Matter**—*G. V. Winters*, D. E. Buckley, Geological Survey of Canada

4:20 (579) **Simplified techniques for the Perchlorination of Polychlorinated Biphenyls in Environmental Samples**—*O. W. Berg*, G. A. V. Rees, M. S. Ali, Ministry of the Environment

4:40 (580) **Stabilization of 1 ppb Hg (II) Solutions stored in Polyolefin Containers**—*R. W. Heiden*, D. A. Aikens, Rensselaer Polytechnic Institute

Friday, March 1

Environmental Analysis—Air Pollution

Friday Morning, Room 235A

J. E. Snodgrass, Presiding

Shenango, Inc.

8:30 (639) **Analytical Chemistry and best available technology for Air Pollution Control**—*R. T. Oliver*, The Foxboro Company

8:50 (640) **An Atmospheric Sulfur Analyzer**—*M. J. Trzeciak*, IBM Corporation

9:10 (641) **Analytical Methodology for the Measurement of Biogenic Sulfur Emissions**—*S. O. Farwell*, University of Idaho, D. F. Adams, W. L. Barnesberger

9:30 (642) **Application of Instrumental Neutron Activation Analysis to the determination of in vitro Solubility of Fly Ash Particles**—*S. H. Weissman*, K. F. McCarty, Lovelace Biomedical and Environmental Research Institute

9:50 (643) **Laser Optoacoustic detection of Ozone, Ammonia and Particulates**—*J. W. Bozzelli*, D. R. Castellano, S. Rosenstark, R. Lee, New Jersey Institute of Technology

10:10 **Recess**

10:20 (644) **ESCA Study of Air Filters**—*J. M. Blaisdell*, G. R. Grieger, Walter C. McCrone Associates

10:40 (645) **A technique for determining the minimum level of a Variable Consistent with a Set of Environmental Data**—*J. L. Fasching*, University of Rhode Island

11:00 (646) **The sampling and determination of Diesel Particulate**—*S. R. Prescott*, T. H. Risby, Pennsylvania State University

11:20 (647) **Determination of Benzo(a)pyrene and Other Polynuclear Aromatic Hydrocarbons in Airborne Particulate Material by Ultrasonic Extraction and Reverse Phase HPLC with Fluorescence Techniques**—*C. Golden*, E. Sawicki, U.S. Environmental Protection Agency

11:40 (648) **Simultaneous Multielement Preparation of Air Particulate Standard Reference Materials and their application in the Intercalibration of Analytical Instrumentation**—*K. W. Olson*, V. A. Fassel, Iowa State University

Sampling hot gases for analysis

Metal Bellows Corp.'s pumping technology has become an industry standard, a laboratory time-saver, and the preferred on-line industrial monitoring technique where contaminant-free and maintenance-free performances are mandatory

The two fundamental necessities for sound operation of analytical instrumentation are a representative, uncontaminated sample and a valid calibration standard. In the pollution monitoring field, regulations often make demands for genuinely difficult analyses of emissions. With today's advanced instrumentation operation at the ppm and ppb levels, an adequate sample handling system is required to prevent contaminated samples and erroneous results.

For the past nine years, the Metal Bellows Corp. (Sharon, Mass. and Chatsworth, Calif.) has pioneered research and development and the application of vacuum pumps and compressors. The company has a standard line of stainless steel bellows vacuum pumps and compressors that meet the challenge of today's instrumentation needs. In fact, all three types of bel-

lows—formed, welded, and metal deposited—are available for a spectrum of products.

Vehicular emissions

The EPA regulation on 1979 certification and test of new heavy duty, gasoline-fueled and diesel engines offers one example where tightening regulations force advanced instrumentation. The present certification standards do not have a separate hydrocarbons requirement. The current standard calls for 16 g/BHP-h for hydrocarbons plus oxides of nitrogen and 40 g/BHP-h for carbon monoxide (CO).

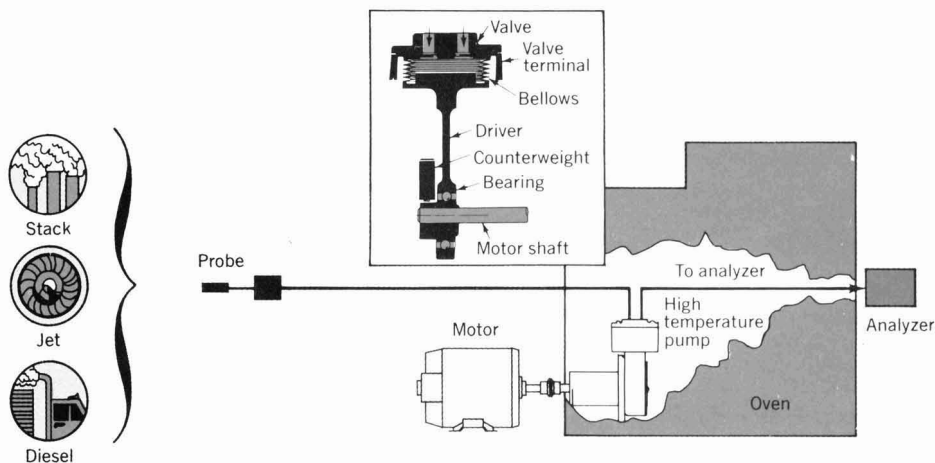
Beginning with the 1979 model year, a separate hydrocarbons requirement has been added to the federal regulations. The standard will be 1.5 g/BHP-h for hydrocarbons, 25 g/BHP-h for CO and 10 g/BHP-h for

hydrocarbons plus oxides of nitrogen.

Metal Bellows' engineer designer Peter Fontecchio says, "heated sample lines, pumps, and components are among the EPA requirements, along with instrument responses of 95% of scale in 6.0 seconds and $\pm 1\%$ precision."

The Process Instruments Division of Beckman Instruments Inc. (Fullerton, Calif.) developed its Model 402 Flame Ionization Hydrocarbon (HC) Analyzer that has been deemed acceptable by the EPA. Beckman Instruments' John Harman, III, says, "a key component of the 402 is a stainless steel bellows pump that provides a clean, hot sample of a high volumetric flow rate to minimize the analyzer/sample line related response times."

Metal Bellows' Fontecchio elaborates. "The heated leakproof sampling



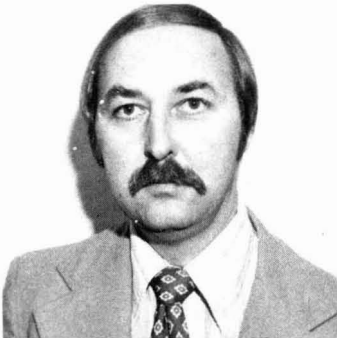
Pumping technology: the key to reliable sample handling. A Bellows' welded pump supplies sample gases at positive pressure and at temperature up to 450 °F to an instrumental analyzer. This pump eliminates the need for oversized vacuum pumps and excessive plumbing and, at the same time, avoids leak problems common in conventional vacuum systems.

system prevents the condensation of hydrocarbons and moisture, and, at the same time, provides contaminant-free gas samples to the monitoring analyzer." He explains that in the Beckman solution, the metal bellows pump delivers the required sample in a hermetically sealed system whose leak tightness is up to 2×10^{-10} He/s. At the same time, measurement repeatability is within $\pm 5\%$.

NO_x and SO_x emissions

Techniques based on the chemiluminescence analysis of nitric oxide (NO) and NO_x (mixtures of NO and NO₂) demand sensitivities as high as 10 ppb. For these applications, real-time monitors of SO₂ and NO_x emissions assess concentrations as high as 2500 ppm.

"Conventional pumping systems become complicated, expensive, and often lead to erratic test results," Fontecchio says. "Interferences from water vapor, residual hydrocarbons, and sulfur compounds influence test reproducibility to a point where the actual test method becomes suspect.



Metal Bellows' Fontecchio
heated samples lines—a new requirement

Problems are also experienced with the chemical interaction of sample handling components with the sample being analyzed."

What they are

Metal bellows pumps have no wearing parts such as piston rings and seals, vanes or diaphragms. They require no lubrication and are unaffected by constant operation. All components, including the stainless steel bellows, valves and drive assembly, are designed to perform in high temperature applications up to 450 °F. These pumps are the ideal choice as the sample handling pump element in the most demanding of today's gas analyses. Additional benefits afforded by the metal bellows pump including constant flow, zero external leakage, long life

with essentially zero maintenance has brought such pumps into use across a wide spectrum of analysis and gas handling applications—from ppb pollution analysis to respirators, and even radioactive gas handling.

More uses

Analytical shortcomings can cost industries their profits. Gas analysis may cost industry dollars, but ignoring the need could cost additional dollars since complete processes, production



Beckman Instruments' Harman
pump used in 402 HC analyzer

lines, even entire industries may be forced to cut back or shut down.

Many different industries including nuclear energy, aerospace, environmental control, automation, and petrochemical are finding cost-effective solutions to their monitoring problems using this metal bellows pumping technology.

Not only for pressure and temperature sensing is this technology used but as actuators, volume compensators, flexible hose and couplings, mechanical feed throughs, accumulators, reservoirs and pulsation dampers, nuclear expansion joints as well as many other devices where absolute leak control, precise operating characteristics, and reliability are mandatory.

The pumps are extremely useful for the instrumental analysis of gaseous pollutants by the following analytical techniques:

- infrared absorption to measure pollutant gases such as SO₂, CO, CO₂, and NO
- light photometry (visible and UV) to measure NO₂, and SO₂
- chemiluminescence to measure NO, NO₂, and NO_x
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CIRCLE 2 ON READER SERVICE CARD

TVA chairman Wagner



Aubrey J. Wagner, chairman of the Tennessee Valley Authority, tells ES&T's Julian Josephson that he started his career with TVA in 1934. He has worked on many and varied projects in engineering, navigation, and international activities. He became a director in 1961, and chairman in 1969. Drawing upon his experience at the helm of the giant government-owned power system, chairman Wagner gives insight into TVA's problems, prospects, and strategies with respect to environmental regulations, and to pollution-abating coal utilization technology for electricity generation.

Mr. Chairman, apparently air pollution laws and regulations will become progressively tighter in the foreseeable future. Do you see these tighter rules as adversely affecting continued conversion to coal use, and expansion of coal use by your own, and perhaps other utilities, for which President Carter has expressed a strong wish? I believe that we are going to have to use more coal in the future, regardless of what the problems are, and probably use it in conjunction with more nuclear power. It is true that increasingly strict requirements for air quality control and other features of coal burning will add to the cost, and therefore the problems of building coal-burning plants. But I think we are going to have to overcome them, because we have to burn more coal whether we want to or not, regardless of what the problems are.

Do you believe that future clean air laws would be a technical impediment to the expanded use of coal by the TVA? I don't see anything in the offing now that would necessarily make it technically infeasible to build coal-burning plants. It is a matter of economics, and the cost that we incur here in our systems, of course, has to be passed on to consumers because there is no other place to find the money to pay for them.

SCRUBBERS

For many years, TVA advocated the use of tall stacks and intermittent controls, rather than scrubbers, for sulfur dioxide (SO₂) reduction. But lately, you have had some initiative of your own on scrubbers, such as at Widows Creek and Paducah. Do you feel that recent court actions will accelerate a trend to scrubbers, and largely put an end to tall stacks/intermittent controls? Well, first let me comment on our position on tall stacks and intermittent control strategy. We

have believed that for a system such as ours, for plants that have up to 25 years of operation on them, and limited remaining useful life; and for plants located in remote areas, intermittent controls plus tall stacks would meet ambient standards at the lowest cost, and we thought that was all that is necessary. We fought that in court to the Supreme Court, and the Supreme Court refused to hear the case. So we lost, and we are now working out with EPA the method that can best be used to meet standards.

But we have experimented with scrubbers. At the beginning of the 1950's we built an experimental scrubber long before anyone else was concerned about clean air, because we could see a problem coming. We also thought it would be useful to recover the sulfur, if we could do it. And as you know, we have a demonstration scrubber beginning operation on a 500-MW unit at the Widows Creek, Ala., plant, so we have long been interested in scrubber technology as one alternative.

If we were building a new plant, we would have to put on a scrubber that would control it; I wouldn't argue with that. We were simply arguing that plants with most of their useful life behind them should not need to put in this expensive technology, because retrofitting it is more expensive and less satisfactory than putting it in initially. Also, it is one thing to say that a scrubber will work to some extent and, therefore, you should go ahead and build one and try it out, and, gradually, improve it.

It is quite another thing to talk about putting a scrubber on every plant in your system right now, because the technology is just not developing that fast. So it is a matter of timing that we are concerned about. I think that scrubbers ultimately will be made to work, but whether they will be the best technology, or whether something else will be better, I don't know. But I think we need to pursue all methods that look promising to clean up coal, so that we can burn it.

LOW-SULFUR COAL

In October, Secretary of the Interior Cecil Andrus said that he wants to see the competitive advantages of western coal, with respect to low sulfur, and, therefore, "best available control technology" [BACT] neutralized through legislation and regulation, so

that eastern coal economy would not be adversely affected. What he said essentially was that western coal, because it is low sulfur, might have this advantage for BACT without use of scrubbers and the like. Would such a policy have any effect on TVA's plans for coal use, or does TVA not plan to use western coal to any appreciable extent? We have said for many years that we don't think it makes any sense to ship western coal to the heart of the eastern coal fields, and use up scarce diesel fuel oil in the process. After all, when we talk about conserving energy, what we are talking about primarily is conserving oil, or natural gas. We aren't helping ourselves if we are using up scarce oil to haul coal around.

The second comment that I would make is that in general, it doesn't seem to me to make sense to control, or to try to override competitive advantages by regulation or legislation. I don't like that general principle. I think things ought to compete on a cost basis, so if there is tremendous difference in the cost of eastern coal, as compared to western coal, I would be concerned about that. Our studies indicate that we can probably control our sulfur output, by using eastern coals at somewhere near the cost of western coals, or, in many cases, cheaper. Therefore, I don't think it will have much effect on us.

FUTURE TECHNOLOGY

A leading expert in the field said that fluidized-bed combustion of coal is now "a proven technology ready for commercial scale-up". If that is indeed the case, do you see fluidized-bed combustion [FBC] playing a significant role in TVA's programs for expanded use of coal, as well as a viable alternative for scrubbers? He said it was ready for "commercial scale-up"? And I don't know that I would disagree with that. In fact, as you may know, we are designing now, or having designed by three different concerns, alternative plans for a 200-MW fluidized-bed plant. Assuming that no "bugs" turn up, we will build one. I would call that a step toward commercial scale-up. But it is a long way from the stage where you are ready to try a new technology to the point where you can buy it as a regular power producer for your whole system, like you now buy coal-burning plants or light-water nuclear reactors.

But we do see it as a possibility for the future. I like the fluidized-bed prospect, because it not only solves your sulfur oxide problem, but apparently solves the nitrogen oxide prob-

lem. And that is a problem that we are going to have to face in the future.

There is another problem of burning coal, or of combustion of any fossil fuel. There are questions about carbon dioxide balance in the atmosphere, and so on. We will ultimately have to face up to those. Fluidized-bed, of course, will not do anything about carbon dioxide, nor will any combustion process that I can imagine. So the problems of coal burning are difficult for the future, but it is essential to have coal available to us. We ought to pursue all possibilities until we find the one that will work the best.

Coal use technology development costs^a

(millions of dollars)

Flue gas cleaning and resource recovery	361
FBC	230
MHD	200
Coal cleaning	75
Fine particulate control	35
Industrial oil / gas use reduction	12

^a Estimated Source: TVA

On the subject of fluidized-bed combustion, approximately how many years off do you see before expanded use of that technology? This is a ballpark figure, and somewhat of an educated guess, but I think it would be somewhere between 10-20 years before you could order a plant, at the very best. And maybe not then. There may be "bugs" in the demonstration process that would need to defer it longer, or make it impossible forever to get such a plant.

Over the longer term, do you foresee TVA becoming very involved with other alternatives to scrubbers, such as solvent-refined coal, or coal-derived clean liquid or gaseous fuels? Yes, I think that TVA will clearly be involved in all of these things. If one of them looks promising, we will be ready to go ahead with demonstration projects in that field. As I indicated, we need to burn more coal. It is important to push all the possibilities that are available to us.

REGULATORY ISSUES

Many critics say that TVA is "dragging its feet" on cleaning up SO_x emissions. We know all too well how they went to court with EPA support.

This does not seem to square with your ambitious plans to move toward commercial scale FBC, magnetohydrodynamics [MHD], coal pre-cleaning, and possible production of fertilizer from scrubber by-products. How would you answer your critics on this score? As I believe I indicated earlier, we approach jobs like this in an effort to do what, in my judgment, is the best for the most people, for the longest period of time. And our "foot dragging" on the scrubber issue happened simply because we thought there was a better way to meet the ambient standards than to go to scrubbers, a way that would be more economical and sure.

In fact, under the first EPA administrator, we got the assurance that we *could* go ahead with intermittent controls and tall stacks, and so we proceeded immediately. It developed that the subsequent administrator changed that position. So we felt that there was a basis for a court test. Well, we don't mind losing a fight. But we don't want to surrender when we think we are right. And this is a case when we fought it out and we lost. So we are now proceeding to meet the emission standards by the best method that we can, and we are trying to hold the cost to a minimum in the process.

Again, I think that our position was misunderstood, because people thought we were talking about tall stacks for everybody, on new plants and everything else. We were simply talking about meeting the standards by the lowest possible cost at our existing plants, many of which were old.

As I've indicated, we are pushing aggressively for new and better technology. But I think people must recognize that it is a long way from an idea that works in the laboratory to a system that will work in all your plants. It is going to take patience and time to work these things out. You can't correct generations of neglect, in relation to our air and water quality, in a few short years. The regulators simply have to recognize that.

Will you still go ahead with the Paducah, Ky., coal washing plant, even though despite a recent court suit, it might mean that technologies will have to be changed and new experimentation be done? Yes, I believe you are talking about our \$150 million coal-cleaning plant. We will probably go ahead and build this plant. It was designed to take care of emission standards of 5.2 lb/million Btu. Coal cleaning will also give us some benefits in our boiler operation, because it takes out more of the dirt, and gives us less corrosion and less erosion problems.

But the indication now is that the 5.2 standard may be changed to 3.5 lb/million Btu. Then, the washing plant alone won't do the job. It will take some partial scrubbing or something else to meet that standard, and we would have to face up to that when it happens.

I think that this illustrates the difficulty that faces not only us, not only the entire utility business, but the American business community generally. Standards change in mid-stream. Uncertainties are the order of the day, and I hear from many businessmen that these uncertainties are preventing them from making investments that they otherwise would be making in plants of various kinds; investments needed to keep the economy moving.

Somehow, our regulatory agencies and our government and legislators have to recognize the difference between an existing plant and a new plant. There should be "grandfather clauses" for existing plants. In addition to that, once standards have been set, they must stay fixed for a while, unless it is very clear that they are inadequate, or that there are some new data that indicate that they are way wrong. Then, of course, they should be corrected.

But changing standards every six months is intolerable, as far as the American business community, the electric utility industry, and TVA are concerned. We don't know what to plan. We have built tall stacks that now are not accepted; we have built electrostatic precipitators that have proved inadequate, because the standards have changed. I have no doubt that the same thing will happen with scrubbers if they are built. We have to maintain some degree of stability—some sense of continuity.

PERSONAL ASIDE

Mr. Chairman, you have had a very long, distinguished, and exciting career in your field, from the bottom all the way up to the top. Officially, you leave office in May. But one such as yourself does not really retire. Do you see yourself engaging in future activities to help to resolve the apparent dichotomy between needs for increased electric power availability and needs for improvement in air quality in the nation? You're right, I've had a long and interesting career in TVA, and I wouldn't swap it for any career that I know of in the world. I've enjoyed every minute of it; it has all been fun, and it still is. As to what I will do when

my term expires in May, I haven't thought a lot about it. I stay busy on the job from day to day and I don't have much time to think about things like that. But I'll remain interested in these things, and if I stay healthy, I will find ways to make my voice heard through a consulting capacity, or in some other way.

The thing that has made TVA interesting is that the nation, in an advancing economy, requires more and more energy, which impacts on the environment, and this conflict comes to focus right here. The TVA board has responsibility both for energy supply and the economy of the region; and for the environment of the region, including clean air and water.



"You can't correct generations of neglect, in relation to our air and water quality, in a few short years. The regulators simply have to recognize that."

TVA chairman Wagner

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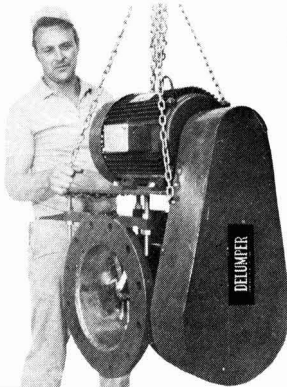
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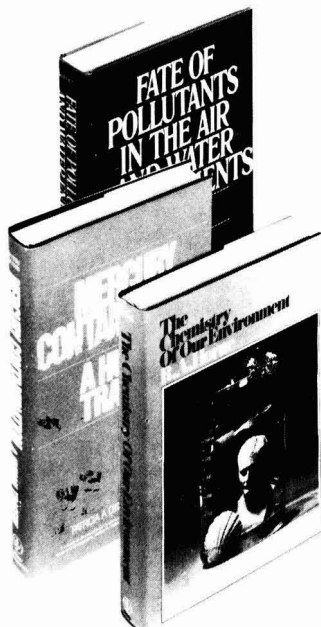
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CIRCLE 3 ON READER SERVICE CARD

Implications of the 1977 Clean Air Act Amendments for stationary sources

A practical explanation of the prevention of significant deterioration and non-attainment policies that affect most major sources in the U.S.

Barbara J. Goldsmith
James R. Mahoney
*Environmental Research &
Technology, Inc. (ERT)*
Concord, Mass. 01742

On August 7, 1977, President Carter signed P.L. 95-95, the Clean Air Act Amendments of 1977. These Amendments impose a wide range of new responsibilities upon the operators of stationary source facilities and substantially change the conditions for obtaining permits for new and expanded plants. Compliance with the Amendments will require development, interpretation and submission of several kinds of technical data and will generally increase the lead time for

obtaining required permits to construct.

This discussion focuses on two sets of provisions contained in the 1977 Amendments: Prevention of Significant Deterioration (PSD) of air quality and Non-Attainment (NA). These provisions impact all new, and most of the existing, major emitting facilities in the U.S.

The language of the Amendments is complex. In some cases, the Act:

- contains multiple definitions of the same term which are applicable to the different provisions in the Act to which sources may be subject

- stipulates interim rules for both PSD and NA until State Implementation Plans (SIP's) are revised to reflect the requirements of the new law and

- exempts some sources in certain cases from the PSD requirements and so forth.

While this discussion covers the principal requirements for stationary source operators wishing to expand or modify existing facilities or construct new facilities in PSD or NA areas, a careful review of the law will generally be required in individual cases and the technical advice of air quality experts should be obtained.

Designation of PSD and NA areas

By December 6, 1977 every state was required to submit to EPA a listing of the attainment status of its Air Quality Control Regions (AQCR's) for each of the six pollutants, for which a National Ambient Air Quality Standard (NAAQS) has been pro-

mulgated. The pollutants are sulfur dioxide (SO₂), oxides of nitrogen (NO_x), carbon monoxide (CO), total suspended particulate matter (TSP), photochemical oxidants, and hydrocarbon compounds. If an area is shown to have air quality better than the NAAQS for SO₂ and TSP (based on air pollution monitoring or modeling data), it will be designated as a Prevention of Significant Deterioration (attainment) area for these pollutants; if air quality is worse than the NAAQS, it will be designated as a non-attainment area. Entire AQCR's may be designated as attainment or non-attainment areas or such regions may be subdivided by the state.

Areas for which there is insufficient information to determine whether the standards have been met will be classified as PSD areas. The final designations promulgated by EPA will have very important influence upon the development of industries within each state. Because attainment/non-attainment designations will be made on a pollutant-specific basis, an industry desiring to construct in a particular area of the country may be subject to PSD rules for one pollutant (for example, sulfur dioxide) and NA rules for another pollutant (for example, nitrogen oxides). The compliance status of AQCR's throughout the country for four of the criteria pollutants based upon 1974 EPA monitoring data is shown in the maps. Since states have been instructed to utilize the most recent data available, the actual designations made by EPA will in some cases differ from the compliance status shown here.

PSD

The 1977 Amendments essentially ratify, extend and generally make more stringent the Prevention of Significant Deterioration provisions promulgated by EPA in December 1974. Three classes of clean air areas are established for which maximum allowable increases in pollution levels for SO₂ and TSP are set. The provisions require that the maximum increases in SO₂ and TSP concentrations throughout these regions not exceed the specified increment limits, which are small percentages of the related NAAQS concentrations for these pollutants. The classes and their allowable air quality increment limitations established in the 1977 Amendments are shown in Table 1.

Facilities commencing construction between June 1, 1975 and August 7, 1977 will be reviewed for a permit according to EPA PSD regulations as promulgated in 1974. The term

Principal EPA rulemaking activities affecting stationary sources

Action	Statutory deadline
• Listing of AQCR's by attainment status	February 1978
• Short-term NO ₂ standard	February 1978
• Stack height regulations (limiting credit to 2½ time the height of the source)	February 1978
• Analysis requirements in PSD areas	February 1978
• Revised NSPS for fossil boilers	August 1978
• Ozone protection regulations	November 1979
• PSD regulations for other criteria pollutants	August 1979
• Visibility protection regulations	November 1979
• NSPS for stationary sources	August 1979– August 1982 ^a

^a EPA is required to list major stationary source categories for NSPS by August 1979 and promulgate NSPS for 25%, 75% and 100% of list by August 1981, 1982 and 1983, respectively.

“commenced construction” means having all permits and having begun a program of continuously preparing a site, or having entered into binding agreements for construction equipment, and the like.

Facilities commencing construction after August 7, 1977 will be reviewed according to the PSD requirements of the 1977 Amendments. However, for these latter facilities the EPA PSD regulations remain in effect until State Implementation Plans (SIP's) are revised to incorporate the PSD requirements of the 1977 Amendments. States are required to complete appropriate SIP revisions by Dec 1, 1978.

The EPA significant deterioration regulations apply to all areas of the country not exceeding the NAAQS for SO₂ and particulate matter in 1974. For consistency, the EPA regulations have been interpreted to include: the Class I area designations, stack height limitations, allowable increment limitations and rules for area redesignations legislated in the 1977 Amendments. Immediately effective changes to PSD requirements are found in the *Fed. Regist.*, Volume 42, No. 212, pages 57459–57462, dated Nov. 3, 1977.

Facilities that had permit applications pending when the Amendments passed or had received preconstruction permits under the EPA PSD regulations but did not commence construction prior to August 7, 1977, are required to undergo a new PSD review based upon the immediately effective modifications described above.

For example, the Edison Electric Institute estimated that about 38 planned units, representing almost 22 000 MW, would require additional review (see *Electrical Week*, October 24, 1977). Once SIPs are revised, all units commencing construction after August 7, 1977 will be subject to the full PSD requirements of the new law. Approximately 143 fossil-fueled steam power units are scheduled to be brought on-line within the five-year period, 1978–1982 (Source: New Capacity Additions Planned or in Construction as of April 1, 1977, *Electrical World*).

Immediately upon passage of the 1977 Amendments, the following PSD areas were designated as Class I areas:

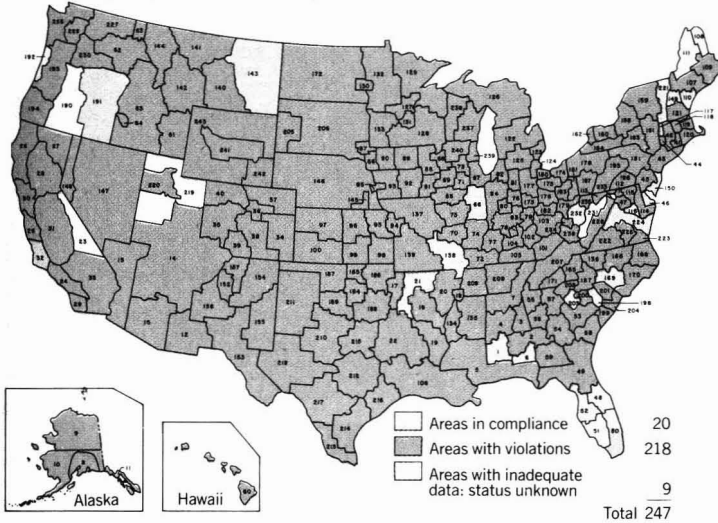
- all international parks
- national wilderness areas
- national memorial parks greater than 6000 acres in size. Areas redesi-

TABLE 1
PSD permitted increments ($\mu\text{g}/\text{m}^3$)^a

	Class I	Class II	Class III	NAAQS
SO ₂ Annual	2	20	40	80
24-hour	8	91	182	365
3-hour	25	512	700	1300(s)
TSP Annual	5	19	37	7560(s)
24-hour	10	37	75	260 150(s)

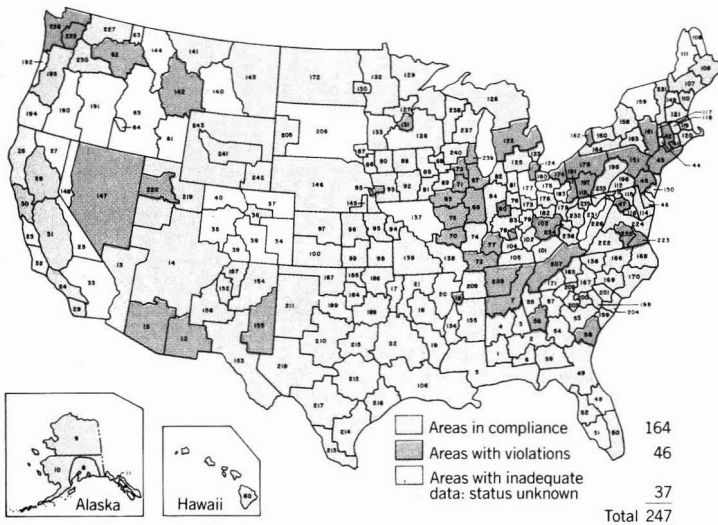
^a All 24-hour and 3-hour values may be exceeded once per year. (s) indicates a secondary standard.

The Nation's 247 air quality control regions Status of compliance with ambient air quality standards for Suspended Particulates^a



^a Based on 1974 EPA monitoring data. This map is based on data contained in the EPA report, Status of Compliance with Ambient Air Quality Standards of Air Quality Control Regions, February 1976. Source: ERT

Status of compliance with ambient air quality standards for Sulfur Dioxide^a



^a Based on 1974 EPA monitoring data. This map is based on data contained in the EPA report, Status of Compliance with Ambient Air Quality Standards of Air Quality Control Regions, February 1976. Source: ERT

ignated as Class I areas under the EPA regulations area also classified as Class I areas under the new Act. (Under EPA regulations, all areas of the country were initially designated as Class II areas; the only area redesignated to Class I is the Northern Cheyenne Indian Reservation in Montana.) All other PSD areas of the country are initially classified as Class II.

A state may redesignate any area to

Class I. States are also permitted to redesignate certain areas to Class III *except* the following areas greater than 10 000 acres in size: present national monuments, primitive areas, recreation areas, wild and scenic rivers, wildlife refuges, lakeshores and seashores, and future national parks and wilderness areas. Redesignation of an area to Class III is a complicated process requiring approval by the governor, public notices and hearings,

consultation with the state legislature and approval by a majority of potentially affected local residents.

Detailed analysis is required prior to public hearing (in the areas to be redesignated and in any area that may be affected by the redesignation), including health, environmental, economic, social and energy impacts of the proposal. Redesignation of areas within Indian reservations may only be done by the applicable Indian governing body.

The EPA Administrator may disapprove a proposed redesignation only if the redesignation does not meet the procedural requirements of the PSD provisions. If federal lands are included in the proposed redesignation area, the Federal Land Manager is to submit recommendations on the proposal, but the state's decision, if it differs, is binding. EPA may be requested to resolve disputes between states and Indian tribes on proposed redesignations.

Increment limitations

Major emitting facilities commencing construction after August 7, 1977 must comply with the PSD numerical increment limitations established in the 1977 Amendments. A "major emitting facility" is defined as one from 28 specifically named categories of industry having emissions of more than 100 tons/year of any pollutant, *and* any other source with emissions of more than 250 tons/year of any pollutant. A listing of the 28 designated industries appears in Table 2.

The short-term (3 and 24 hour) SO₂ and TSP increments in any Class I, II, or III area (shown in Table 1) may be exceeded one per year. The increment limitations represent allowable concentrations above baseline measurements of air quality. "Baseline air quality" is defined as the concentration level existing at the time of the first application for a permit in an area subject to the PSD rules.

Determination of baseline air quality is to be assessed by using available air quality data from EPA or a state air pollution control agency and using monitoring data that the permit applicant is required to submit. The baseline air quality concentrations must include all projected emissions from any major emitting facility that commenced construction before January 6, 1975, but which has not begun operation by the date of the baseline determination.

SO₂ and particulate emissions from any major emitting facility that commenced construction after January 6,

1975 cannot be included in the baseline but must be counted against the maximum allowable increment limitation for the applicable PSD area.

The governor of a state can exempt the following cases in determining compliance with the allowable PSD increments:

- increases in ambient concentrations owing to fuel conversion orders
- conversion from natural gas to coal resulting from a curtailment of supplies
- increases in particulate concentrations resulting from construction or other temporary emission-related activities
- sources outside the U.S. Discounting the contribution of pollutants from coal, conversion projects (conversion of a fuel-burning facility to the use of coal) will be for a maximum of five years.

In order for an existing or proposed major emitting facility to be modified or constructed in any of the three areas, the facility must:

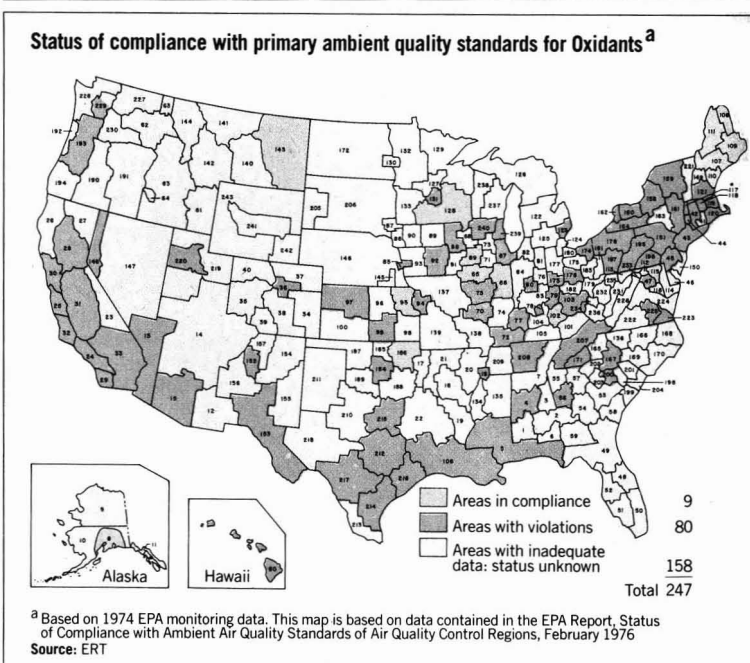
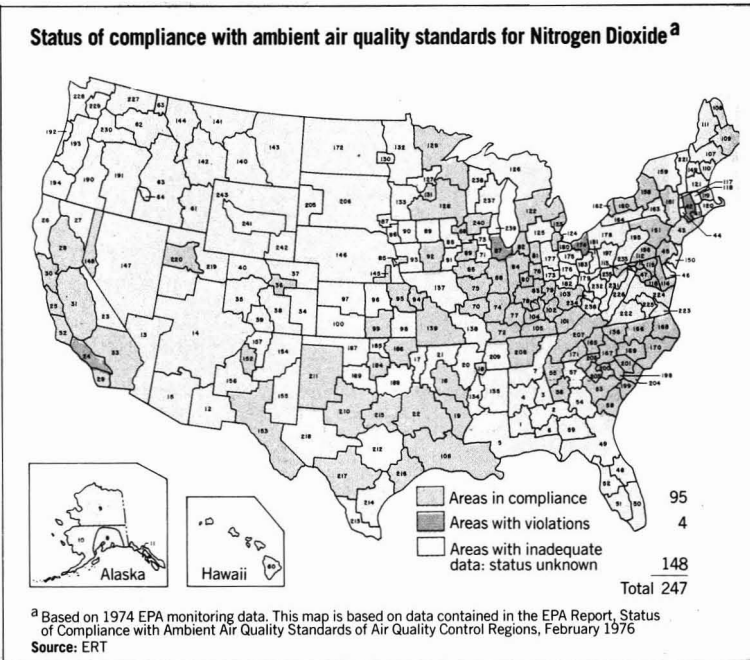
- have obtained a permit (preceded by an extensive analysis of impacts and public hearing)
- not exceed or cause exceedance of the applicable increases in pollutant concentrations allowed
- agree to conduct whatever monitoring is necessary in any area potentially affected by emissions from the source and use Best Available Control Technology (BACT).

BACT is to be determined on a case-by-case basis for each pollutant subject to regulation under the Clean Air Act and must represent an emission limitation based on the maximum degree of reduction (taking into account energy, environmental and economic impacts) which the permitting authority determines is achievable for a specific facility. All sources in the country, regardless of where the plant is located, are also subject to New Source Performance Standards (NSPS), expressed as emission requirements for the applicable source category.

Foremost among the questions of interpretation is the issue of the permitted one excess per year.

Based upon preliminary EPA guidance materials, it appears that the increments may be exceeded once per year at each location (receptor site) surrounding a proposed facility, rather than permitting only a single excess anywhere in the region surrounding the facility. Clearly, the former approach is less restrictive than the latter.

This leads to another important issue: the "sharing" of PSD increments



among adjacent or nearby sources. It is important to note that the increment limits must be attained for all future times; therefore, individual new facilities will not generally be permitted to "use up" the increment. Generally the sharing of the PSD increments will result in lower permitted emission rates for each facility than would be the case if a facility were evaluated independently of its potential future industrial neighbors.

A related issue to be resolved is the separation distance that will be required between facilities before the impacts of each facility can be considered independently rather than additively. The production capacity and size of a facility may have to be reduced, or stringent controls required, depending on interpretation of these and other issues in regulatory practice.

These issues may become even more

TABLE 2

Major stationary source subject to PSD review**Power plants (>250 million Btu/h)****Specific sources (>100 tons/y any pollutant)**

Power plants	Coke oven batteries
Coal cleaning plants	Sulfur recovery plants
Kraft pulp mills	Carbon black plants (furnace process)
Portland Cement plants	Primary lead smelters
Primary zinc smelters	Fuel conversion plants
Iron and steel mill plants	Sintering plants
Primary aluminum ore reduction plants	Secondary metal production facilities
Primary copper smelters	Chemical process plants
Municipal incinerators >250/tons/day	Fossil-fuel boilers >250 million Btu/h
Hydrofluoric acid plants	Petroleum storage and transfer facilities >300 000 bbls
Sulfuric acid plants	Taconite ore processing facilities
Petroleum refineries	Glass fiber processing plants
Lime plants	Charcoal production facilities
Phosphate rock processing plants	

Any other source (>250 tons/y any pollutant)

pronounced when PSD rules are promulgated for the other criteria pollutants. EPA is required to promulgate PSD regulations governing carbon monoxide, hydrocarbons, oxides of nitrogen and photochemical oxidants by August 1979. Because of the complexity of chemically reactive pollutants, the control of such pollutants in relation to PSD will likely preclude the use of the air quality increment concept employed with SO₂ and TSP.

Exceptions—Class I areas

The protection of "air quality-related values" is a key factor in determining whether a facility may be granted a permit when it would impact a Class I area. If the Federal Land Manager finds that emissions from a proposed facility would have an adverse impact on the "air quality-related values" of the land area (even if allowable Class I increments would not be exceeded) a permit cannot be issued unless the source can demonstrate that no adverse impact would occur.

If, however, the emissions from the facility would not adversely impact

these values but would exceed the Class I increments, the state may issue a permit which would allow the facility to comply with less stringent air quality increments. (Even in this case the maximum increments are the Class II values, except for the three hour SO₂ increment limit that is not to exceed 325 µg/m³).

If a permit is denied in this procedure, the facility owner may demonstrate to the governor after public hearing that the facility cannot be constructed in a Class I area and comply with the Class I increments. The governor may then permit the facility to exceed the short-term Class I SO₂ increments on 18 days a year if the Federal Land Manager concurs.

If the Federal Land Manager disagrees with the proposed variance, the final decision is made by the President, based on the "national interest". If a variance is granted, the emission of SO₂ from the source together with all other sources, may not exceed the maximum allowable increases over baseline concentrations on these 18 days as shown in Table 3.

In all cases, the facility owner/operator must still demonstrate that the variance will not adversely affect the air quality-related values of the Class I area. No similar variance is allowed for the increment limit in Class II or Class III areas.

Visibility

It should be noted that visibility is the only "air quality-related value" that is specifically cited in the 1977 Amendments. Although it is likely that potential adverse impact on visibility will act as the primary "trigger mechanism" governing variances from the stated Class I increment limits, other "values" might include odor, vegetative stress, climatic change and so on.

Visibility protection has emerged as a major issue in the 1977 Amendments, and EPA is required to promulgate regulations on visibility protection by August 1979 to enforce a national goal of visibility protection. Existing sources in operation for less than 15 years may be required to retrofit control technology if they are shown to contribute to visibility impairment.

Non-attainment

Construction permits for major new and modified stationary sources in non-attainment areas will be issued in accordance with EPA's December 1976 Interpretative Ruling on emission offsets until July 1, 1979, unless the state obtains a waiver to this policy. States may be granted a waiver if they have a detailed emission inventory of sources, an enforceable permit program, and have a plan for reducing overall emissions.

Major sources subject to this ruling include any sources that emit, or have potential to emit, 100 tons a year of any pollutant, including any source of fugitive emissions. The emission offset policy requires that a new or modified source must meet the following conditions before a permit can be granted:

- The plant must obtain an "emissions offset"—emissions from existing sources in the region must be reduced in an amount more than sufficient to offset the new plant's emissions.

- The plant must attain an emission limitation that is the Lowest Achievable Emission Rate (LAER).

- The emission offsets obtained must produce a "positive net air quality benefit" resulting in "reasonable further progress" toward attainment of the applicable standard.

- All the applicant's existing facilities within the AQCR must be in

TABLE 3

SO₂ increment limits for 18 exceeding days in a Class I region^a

Period of exposure	High terrain areas	Low terrain areas
	(900 ft above stack base)	
24-hour maximum	62 µg/m ³	36 µg/m ³
3-hour maximum	221 µg/m ³	130 µg/m ³

^a A 3-hour and 24-hour exceedance occurring on a single day or two or more 4-hour violations occurring on a single day constitutes one exceedance day.

compliance with applicable emission limitations or standards.

Emission offsets are determined on a case-by-case and pound-per-pound basis with reductions required to exceed new emissions when all facilities are operating at maximum load. "Banking" of unused offset credits is not permitted, but credit may be obtained, in limited conditions, by the permanent shutdown of an existing source.

After June 30, 1979 each state must have revised its SIP to provide for attainment of primary ambient air quality standards by December 31, 1982 before a major new source may locate in a non-attainment area. For areas with photochemical oxidant or carbon monoxide non-attainment conditions an additional five-year extension is available to December 31, 1987.

Since new sources must be included in the SIP it will generally be to the advantage of new source operators to communicate development plans to the applicable state permitting authorities as soon as they are known.

Data, modeling & monitoring

Owners of all existing stationary sources of pollution have several specific responsibilities for compliance under the 1977 Amendments. Generally, compliance will require conformance with several provisions of the SIP and will require periodic reporting of such conformance to the state agencies.

In regions designated as non-attainment areas, even those industries presently in compliance will frequently have new requirements for additional controls imposed to bring about compliance in the area. The long time scales required for planned changes or facility modifications under the provision of the 1977 Amendments make it imperative that periodic short- and long-term planning of compliance with the Amendments be carried out by all major industrial operators.

Owners of planned new facilities, or facilities undergoing substantial modification, will face all the requirements imposed upon existing facilities. These owners will also have requirements for development and submission of the necessary permit applications.

Supporting data for such applications will include specific evaluation of the PSD or non-attainment area status of the new operation and will include reports of baseline monitoring at the proposed site of the new activities. Time schedules required for the development of all the supporting data

TABLE 4

Monitoring requirements for issuance of permits

Activity	Time required	Cumulative
Specify monitoring required	1-2 months	1-2 months
Select vendors and contractors	1-3 months	2-5 months
Procure and install equipment	1-4 months	3-9 months
One-year baseline monitoring	12 months	15-21 months
Complete data analysis and modeling	1-4 months	16-25 months
(Permit application complete)		
Request special model, with agency hearing and review (if necessary)	2-6 months	18-31 months
Hearings on application and final agency review	3-12 months	21-43 months

will be lengthy in many cases, and will require detailed advance planning for new facilities.

The review and permitting process under the PSD provisions involves the use of air quality modeling for estimating the impact of facilities not yet built. Therefore, in these cases, the model formulation, data used, and interpretation of the model results will be direct determinants of site suitability and emission limits required for industrial sites.

In particular, since the short-term PSD increments can be exceeded only once a year, models must be used to evaluate the meteorological or topographical conditions in a region that has the highest expected concentrations of pollutants.

The use of special models necessary to accommodate unique terrain or meteorological features of an area may be allowed by the EPA Administrator following notice and public hearing. In the case of non-attainment plan development, models are also used to evaluate the air quality benefits to result from various emission reduction alternatives, including evaluation of allocation of emission reductions among multiple sources in a region.

By February 7, 1978 EPA is required to promulgate regulations specifying requirements for the evaluation of facilities proposed in PSD areas, including the models to be used. The time sequence of this and other major EPA rulemaking activities that are required under the 1977 Amendments are shown.

Beginning in August 1978, air quality monitoring will be required as part of the permit process. This requirement can be waived or shortened if the state determines that adequate data already exist or a shorter period

will be adequate to document baseline conditions.

For new facilities and modification, the requirement to submit one year of baseline monitoring data as part of a permit application causes a substantial lengthening of the total time required to achieve issuance of a permit. The time estimates indicated in Table 4 are illustrative only, and may in fact be underestimates in several cases.

Even with maximum efficiency achieved in the planning and implementation of a monitoring program, the time required to achieve a permit approval will likely be as long as two years. Considerations of this time schedule suggests that an early start of baseline monitoring may be appropriate for many facility owners, in advance of the development of specific plans for facility expansions or modifications.



Barbara J. Goldsmith is manager of ERT's Office of Environmental Policy. She has served as technical project manager for most of the national studies that ERT has performed for industry & government clients pertaining to the effects of the significant deterioration provisions.

James R. Mahoney co-founded ERT in 1968. Since then, ERT has grown into a full service environmental company with 700 persons in facilities across the U.S. During the past seven years he has appeared as an expert witness in numerous regulatory and legal proceedings involving environmental and energy issues.

A Navy expert explains why and how x-ray spectroscopy works, and can be a cost-effective analytical technique for

PINPOINTING AIRBORNE POLLUTANTS

L. S. Birks

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Washington, D.C. 20375*

Any analyst who has not seen a modern x-ray spectrometer perform its magic should certainly seek an opportunity to do so. You insert a piece of filter on which particulate pollutants have been collected, push the start button, and instantly the x-ray spectrum of the major constituents begins to grow on the live-time display. You wonder if that strong line is zinc, so you push the "3" and "0" keys on the console for the atomic number of zinc, and marker lines with the symbol Zn appear at the proper place on the display screen. If you guessed wrong, simply type in the atomic number for any other element, and those markers replace the Zn markers. After a minute or two, most of the minor constituents, as well as the majors are visible, and you can do a quick semi-quantitative estimate by "eyeball".

Want to compare the present spectrum with something collected earlier? Just call the earlier spectrum from memory in the mini-computer, and it is displayed overlaid on the new

spectrum (some instruments do it in color!). Want a record of just what the new sample contained? Press another button, and out comes hard copy listing each element, its x-ray intensity, and the estimated amount in $\mu\text{g}/\text{cm}^2$ on the filter, as scaled from calibration standards measured previously and stored in the computer memory.

How it all came about

Less than six months after the Environmental Protection Agency (EPA) was established in 1970, work began on the development of x-ray fluorescence techniques specific to particulate pollution analysis. Initial objectives were to:

- establish detectable limits and sensitivity for all elements of interest in air pollution studies
- develop optimum specimen treatment techniques for various kinds of specimens of interest
- examine possible x-ray line interferences
- establish cost-per-sample data for both large and small numbers of samples.

The objectives were achieved quickly, because the x-ray technique turned out to be a "natural" for the

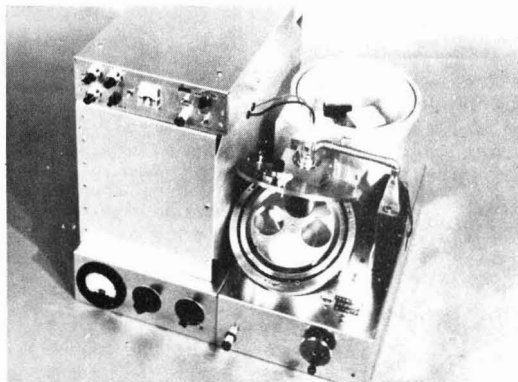
pollution samples. The reasons for this are perhaps obvious on hindsight: Concentrations of interest in particulate air pollution are of the order of $\mu\text{g}/\text{m}^3$, and the x-ray method is sensitive enough to detect less than $1 \mu\text{g}$ of most elements.

Thus, suitable samples can be collected by simply filtering the particulates out of about a cubic meter of air. Filters such as Whatman paper, Millipore, Nuclepore, and the like, are well suited as sample mounts because they have low impurity content to interfere with element identification, and their low mass minimizes x-ray scattering (background).

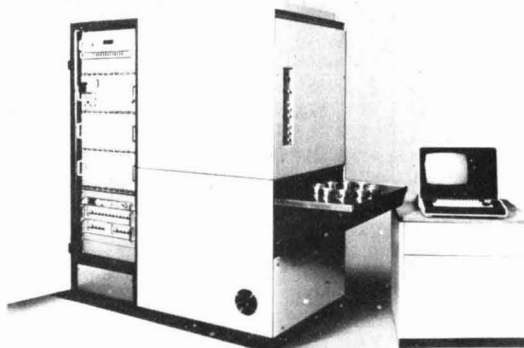
Also, the nondestructive nature of the x-ray method means that the samples can be saved after measurement and used as legal evidence for prosecuting polluters. Thus, within the few short years after the initial work, many laboratories, using a variety of x-ray techniques, were participating in pollution analysis.

A variety of techniques

The important variables in x-ray fluorescence analysis are the source of excitation, the specimen geometry, and the method of measuring the emitted



Analyzer. *Determines sulfur in field*



Sophistication. *Analyzes many pollutants at once*

x-ray spectrum. Selecting the optimum combination of these variables for the pollution analysis problem is still somewhat of an area of controversy within the x-ray community, but the principles are simple, and easy to elucidate. The least controversial of the variables is specimen geometry, because it was recognized early in the pollution work that background intensity (noise) must be kept low in order to detect the signals from the small concentrations of pollutants collected. Such noise is directly proportional to the mass of the filter; hence the desire for filters of minimum mass. The other two variables require more discussion.

Any quantum (particle or radiation) of sufficient energy can excite the characteristic x-ray spectrum of an element. Electrons are of little use for pollutant particles spread out on the surface of a filter, because the strong bremsstrahlung (x-ray spectrum continuum) intensity generated in the filter completely swamps the characteristic lines from the pollutant elements.

Protons or alpha particles of suitable energy do not generate a measurable bremsstrahlung, and generally give a slightly better detective limit than other sources. However, the accelerators (Van de Graaffs or cyclotrons) necessary to generate the positive ions are building-sized instruments, and very expensive to purchase and maintain. Therefore, ion excitation is done only at nuclear physics laboratories that already have such accelerators available.

All of this leaves primary x-radiation as the most common source for exciting the characteristic x-ray spectrum of the sample. For such radiation, the radioisotopes nowadays come in a variety of emissions, and do not require a power supply; but they cannot compete with the 2-3-kW x-ray tubes

where high output is required. Thus, where low power is adequate, low-power x-ray tubes have replaced isotopes. So the x-ray tube, high powered or low powered, remains as the source of choice for over 90% of the pollution analysis done.

X-ray spectra

Each characteristic x-ray line from an element can be expressed in terms of its wavelength, or, equivalently, in terms of its energy. This leads to two alternative means of measuring a spectrum: wavelength dispersion, or energy dispersion.

The x-ray tube (or the fluorescer) excites the x-ray lines from the sample elements; they are emitted in all directions. In wavelength dispersion, the characteristic emission is limited to a parallel bundle by a collimator, and diffracted, one wavelength at a time, according to the setting of the analyzer crystal (Bragg's law). As the crystal and detector are rotated, the spectrum lines are measured sequentially.

On the other hand, in the case of energy dispersion, the detector (usually a solid-state silicon device) is energy sensitive, so each time it absorbs a characteristic x-ray photon, it emits a pulse whose amplitude is proportional to the energy of the absorbed photon. Therefore, there is no need for physical separation of the lines.

Each pulse from the detector is stored in a multi-channel analyzer according to the pulse amplitude; thus, the measurement is for all x-ray lines "simultaneously", and the operator can watch the collection of the spectrum as it occurs. A comparison of energy dispersion and wavelength dispersion in Figure 1 illustrates the considerably better resolution of the wavelength spectrum, but what is not shown is the considerably longer time to gather the information.

The ultimate in x-ray instrumenta-

tion for large-scale analysis of pollution samples is the multiple-crystal spectrometer, Figure 2. In this \$150 000-\$200 000 instrument, each crystal and its detector is optimized for a particular element. This means that 20 or 30 elements of interest can be specified in advance. In addition, the instrument may contain either a scanning crystal-spectrometer, which can measure any element not on a fixed channel, or an energy-dispersion channel which detects all the elements present.

There are very few line interferences because of good resolution. High-speed results from the simultaneous measurement of essentially all elements of interest. The large number of samples that can be measured per year makes the cost per sample (including capital-investment amortization) less than that for other instruments.

Wavelength or energy dispersion each has certain advantages. For large-scale analysis, when most of the elements of interest can be specified in advance, the multiple-crystal spectrometer offers the best sensitivity at lowest cost per analysis. On the other hand, when the elements of interest cannot be specified, energy dispersion offers acceptable sensitivity and coverage of almost all elements for a lower capital investment, but with a penalty of more line interference (because of poor resolution) and longer analysis time. The sequential crystal spectrometer is a fine laboratory instrument that can match energy dispersion in coverage of all elements, but with a severe penalty in analysis time.

Quantitative results

"Eyeballing" the spectrum in Figure 1 gives the analyst a considerable amount of semiquantitative information. Barium seems to be at a much higher concentration than iron, for example. But eventually, one wishes to

Why x-ray fluorescence analysis works

Each element emits characteristic x-ray lines when it is excited by high-energy particles. These particles can consist of electrons, protons, or ions, for example. Radiation, such as short-wavelength x-rays, can also excite elements. The characteristic lines which the elements then emit are measured by crystal spectrometers, or energy-sensitive detectors, to determine their wavelength and intensity. The wavelengths identify the elements, and the intensities are

proportional to the concentrations on a filter, usually expressed as $\mu\text{g}/\text{cm}^2$. This technique has certain advantages:

- There are few line interferences because there are only a few x-ray lines per element.
- Sensitivity and limit of detection are relatively constant over large ranges of atomic number.
- The spectrum of an element is independent of the physical state or chemical combination of the element, but high resolution x-ray spectroscopy can be used to distinguish va-

lence state for some elements, such as sulfur.

• Except for elements of lower atomic number than that of fluorine, there are no "blind spots" in the periodic table, as there are for atomic absorption, in which it is difficult to prepare hollow-cathode lamps for some elements.

X-ray tubes represent the best combination of capital investment and capability. By contrast, radioisotopes require no power supply, but their output is extremely limited, by comparison, to that of x-ray tubes.

express each element quantitatively in terms of $\mu\text{g}/\text{cm}^2$ on the filter. To accomplish this, there are a few simple, but necessary factors to consider.

One is background intensity. Only the x-ray line intensity above background represents the elemental concentration; thus, the background must be subtracted before any data interpretation can be done. Fairing in the background manually is adequate where the lines are sufficiently intense and do not overlap each other. How-

ever, it has become more commonplace to use mathematical functions to represent the background, and to do the subtraction automatically for the whole energy spectrum. Knowing the background is necessary if quantitative estimates of line intensity are to be obtained.

Another factor is sensitivity. Calibration for pollution analysis is generally done with standards of the individual elements. The standards may be evaporated films, precipitates from

known solutions, or any suitable deposit of $10\text{--}100\ \mu\text{g}/\text{cm}^2$ concentration. For such low concentrations, the x-ray intensity of the characteristic lines is linear with concentration. Sensitivity is expressed, for instance, as counts—that is, x-ray photons detected—per 100 seconds/ μg per cm^2 , or some other suitable notation. The sensitivity, along with the background intensity, determines the limit of detection for an element.

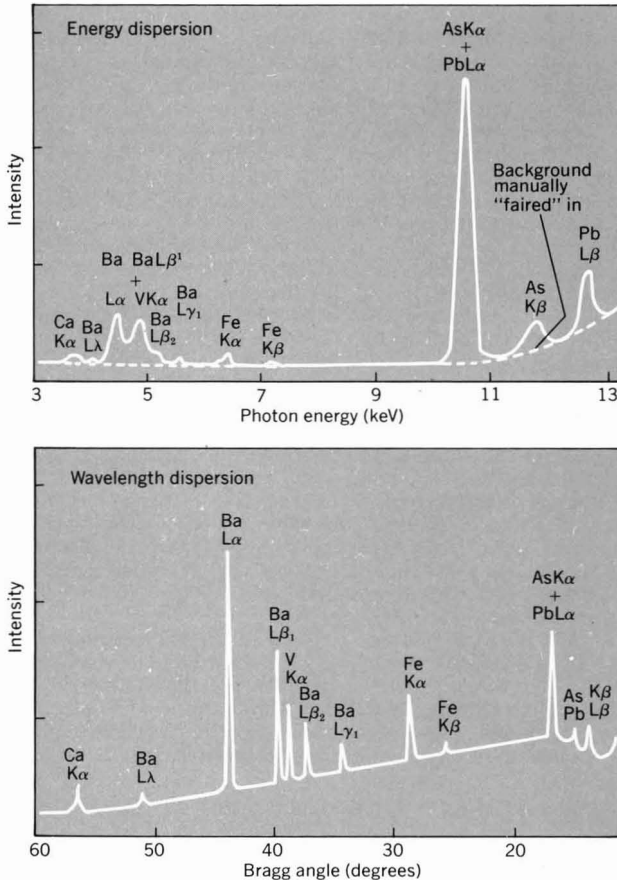
Particle-size effects must also be taken into account. As was stated earlier, the calibration curves are linear for the low average mass per cm^2 concentrations present in pollution samples. However there may be absorption effects within large individual particles. These effects are easy to correct for any assumed particle size and composition. These effects, as well as those of line interference, are defined mathematically.

Because of the available tabulations of x-ray parameters such as scattering coefficients, fluorescent yield, and the like, it is possible to predict absolute sensitivity and limit of detection values without ever making a measurement. This rather unique feature of x-ray fluorescence analysis allows management to determine what kind of equipment is best for a given application. It also allows the analyst to judge the best x-ray tube to use, or how long a counting interval will be needed to measure the sample.

The near future

The improvement of analytical instrumentation and techniques is a never-ending task, because demands always stay ahead of capabilities. Among these improvements are new directions in x-ray fluorescence analysis of pollution samples. These entail

FIGURE 1
Element spectra . . .



. . . and a system that determines them

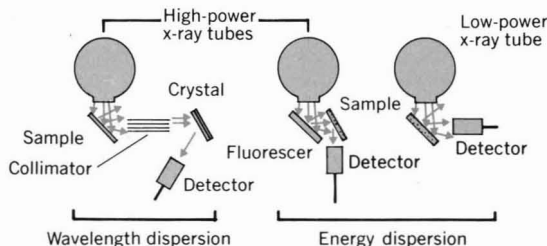
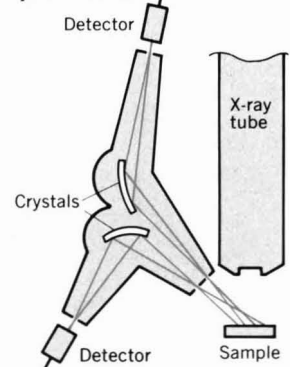


FIGURE 2
New multiple-crystal spectrometer



the measurement of valence state for some elements, and the extension of analysis to soluble elements in water samples.

X-ray lines are essentially independent of the chemical compound in which an element is present. However, high-resolution x-ray spectroscopy can sometimes distinguish valence state, if it is the deliberate intent of the analyst to do so. Sulfur is an example of an element for which it is important to know the valence. If sulfur is present as a sulfate, it probably came originally from SO_2 , an undesirable pollutant. But if it is present as a sulfide, it probably represents relatively innocuous mineral dusts.

Detailed S $K\beta$ spectra for sulfate and sulfide forms are shown in Figure 3. By measuring the ratio of intensity at the positions marked A and B in Figure 3, one can calibrate the sulfate fraction as shown in Figure 4. In practice, total sulfur can be determined from the S $K\alpha$ intensity; the sulfate fraction is then determined from the ratio curve in Figure 4.

Two special sulfur-measuring instruments are being prepared for the

EPA laboratory in Raleigh under an interagency agreement with Naval Research Laboratory (NRL). One is a replacement channel for the multiple-crystal spectrometer instrument; it will be used for routine sulfate determination. The other is a portable vacuum crystal spectrometer, which uses a 50-watt transmission-target x-ray tube. Although this latter instrument is primarily intended for sulfur measurements at suspected pollution sites, the scanning spectrometer can also be used to analyze for phosphorus, chlorine, or other elements.

Measurements in water

Particulate matter in water can be filtered out and measured in the same way as in air samples, but elements in solution require chemical preconcentration. For these purposes, ion-exchange resins have been used successfully for many x-ray applications, but water analysis poses special problems. For instance, calcium (Ca) and magnesium (Mg) are likely to be present at tens of mg/L. They compete strongly with trace metals present at $\mu\text{g/L}$ levels for the ion-exchange sites on most resins. Specific ion-exchange resins have been developed for certain groups of elements, but such specificity defeats the multi-element capability of the x-ray technique. However, precipitation with ammonium pyrrolidine dithiocarbamate (APDC) or coprecipitation with iron hydroxide have been successful in some water pollution analyses.

At NRL, a current program, supported by the EPA laboratory in Athens, Ga., is investigating the use of a combination of two reagents (polyvinylpyrrolidone and thionalid) to precipitate a number of elements from water. Preliminary results show promising recovery rates at the 10 $\mu\text{g/L}$ level in the presence of 50 mg/L of Ca, and 10 mg/L of Mg. If a liter of water is used, and if the present recovery rates are maintained at even lower concentrations, the estimated detection limit for collection on a 10-cm² area of filter would be 0.1 $\mu\text{g/L}$ for favorable elements.

Heightened awareness

Although the demand for pollution analysis has not resulted in the discovery of any new principles in x-ray fluorescence, it has certainly helped make many more analysts aware of x-ray capabilities. Fortunately, x-ray parameters and methods of data interpretation were well known from previous x-ray applications.

All of the factors and calculations

described in the section above on quantitative analysis can be treated with nothing more complicated than a slide rule or pocket calculator, if one wishes. Nevertheless, they can also be programmed for a mini-computer, with resulting automation and savings in time. The ability to predict absolute sensitivity and limits of detection from first principles is a feature not shared by many other analytical techniques; it allows the selection of optimum equipment and measuring strategy at low cost, and in advance of any experimental measurement.

Measurement of valence state and chemical combination will probably come to be regarded as necessary in the future, when more is known about health effects. Not all elements of interest will be as easy to determine as sulfur is, in terms of valence measurements, but work will be under way within a year or two to ascertain problems and limitations for other elements.

The application of x-ray fluorescence to pollution analysis has been rewarding in terms of low cost quantitative analysis. However, it is to be hoped that the scientific capability to measure nearly everything of everything will not be used as an excuse to do so!

Additional reading

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L. S. Birks is head of the X-Ray Optics Branch at the Naval Research Laboratory. He has authored books on x-ray spectrochemical analysis and electron probe microanalysis, as well as numerous journal articles on x-ray-related subjects. His work on environmental samples has been done under an interagency agreement with the EPA.

Coordinated by JJ

FIGURE 3

Sulfur valence spectra

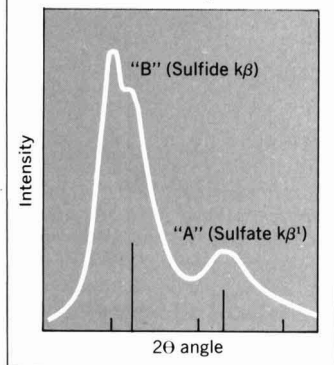
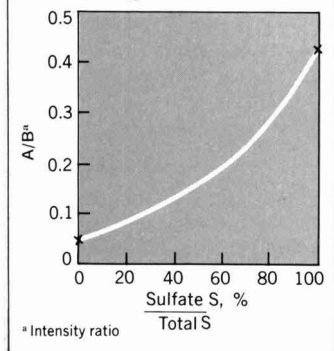


FIGURE 4

Determining sulfate fraction



Controlling the entrance of toxic pollutants into U.S. waters

While the primary statutory authority is the Federal Water Pollution Control Act Amendments, eight other federal laws may be called upon to protect the water environment

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It is becoming increasingly clear that control of toxic pollutants will be receiving more and more emphasis in the near future. There is an impressive array of federal statutes that can be invoked to control the entry of toxic pollutants into our Nation's waters.

Some of these laws explicitly require coordination with actions taken under other federal laws (for example, the Toxic Substances Control Act), but there remain areas of potential duplication such as the overlap between the Federal Water Pollution Control Act (FWPCA) and the Marine Protection, Research, and Sanctuaries Act relating to ocean discharges.

The FWPCA provides a broad spectrum of mechanisms for the control of toxic pollutants. Other federal laws are more narrowly drawn and focus on one aspect such as transportation. Some focus on protection from types of pollutants such as pesticides or radioactive wastes, while others focus on protection of types of waters such as drinking water or the oceans.

It is suggested that the weakest areas in the control of toxic pollutants are from accidental spills, and from non-point sources such as urban runoff. However, further implementation of Section 311 of the FWPCA may result in a greater reduction of spill episodes. Section 208 requires planning for the control of nonpoint source pollutants, but does not provide explicit control mechanisms other than those which may be developed by state and local authorities.

This paper examines the federal statutory authorities available for the control of toxic pollutants in the aqueous environment.

The following statutes are examined and discussed:

- Federal Water Pollution Control Acts
- Marine Protection, Research, and Sanctuaries Act of 1972
- Safe Drinking Water Act of 1974
- Resource Conservation and Recovery Act of 1976
- Hazardous Materials Transportation Act of 1974
- Ports and Waterways Safety Act of 1972
- Federal Insecticide, Fungicide, and Rodenticide Act of 1972
- Toxic Substances Control Act of 1976
- Atomic Energy Act of 1954.

Figure 1 shows how each of these laws relates to the control of toxic pollutants in the water environment.

There are other statutes that may indirectly help to control the entry of toxic pollutants into water, but are not discussed in this paper. These include, but are not necessarily limited to, the Clean Air Act, the Occupational Safety and Health Act, and the Federal Food, Drug and Cosmetic Act.

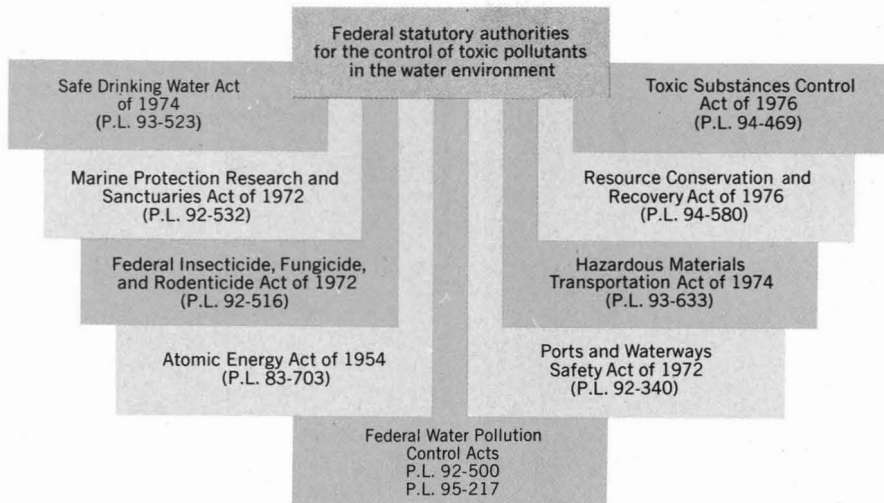
The water pollution control acts

The FWPCA and recent amendments to the act are the principal mechanisms for the control of water pollutants

Section 307(a), Toxic Pollutant Effluent Standards, requires the EPA administrator to publish a list of toxic pollutants for which an effluent standard will be established. Before the recently enacted amendments, procedural and legal difficulties tied up this regulatory mechanism in an administrative and legal quagmire. Only six chemicals have been regulated.

FIGURE 1

The water acts and their interaction with other federal laws



In 1973, a list of nine toxic pollutants was published, and standards were proposed. The nine pollutants were aldrin/dieldrin, benzidine, cadmium, cyanide, DDT (DDE, DDD), endrin, mercury, PCBs, and toxaphene. At the required hearing, EPA could not justify the proposed standards on the record of the hearing, nor could revised standards be justified.

In 1976, EPA repropoed standards for the four pesticides, benzidine, and PCBs. Standards for the six pollutants were promulgated in early 1977. Formulation of aldrin/dieldrin, DDT (DDE, DDD), and PCBs was prohibited outright, as were discharges of endrin and toxaphene from formulators. Benzidine dischargers, and manufacturers of endrin and toxaphene were required to meet standards based on the best available technology.

Under the new amendments (Clean Water Act of 1977, P.L. 95-217), methods for establishing toxic pollutant standards are simplified by specifying a less formal rule-making procedure, and the period for compliance has been extended from one to three years as long as there is no significant risk to public health, water supplies, or the environment. The legislation also added the list of 65 toxic chemicals and classes of chemicals from a settlement agreement (discussed later) to the Section 307(a) list.

Section 311, Oil and Hazardous Substance Liability, provides for the designation of hazardous substances which, when discharged (including spills), present an imminent and substantial danger to the public health or welfare, and for penalties for discharges of such hazardous substances from onshore and offshore facilities and vessels. No hazardous substances have yet been designated under this section, but a list of some 300 chemicals has been proposed by EPA.

Section 311(c) further directs that a National Contingency Plan be developed to provide for efficient, coordinated, and effective action to minimize damage from oil and hazardous substance discharges, including containment, dispersal, and removal of oil and hazardous substances.

The recent amendments extend to 200 miles the juris-

dition of Section 311 regarding discharges of oil or hazardous substances in connection with activities under the Outer Continental Shelf Lands Act, or the Deepwater Port Act of 1974, or which may affect natural resources belonging to, appertaining to, or under the exclusive management authority of the U.S. (including resources under the Fishery Conservation and Management Act of 1976).

Section 301 and 304, Effluent Limitations and Guidelines, stipulate that technology-based effluent limitations and guidelines are required for all pollutants, including toxic substances, from point-source discharges. These limitations are to be accomplished in phases. The first phase required "best practicable control technology" (BPT) for industry, and "secondary treatment" for municipal dischargers by July 1, 1977. An estimated 85% of industrial dischargers and 35% of the cities met this deadline.

The new amendments provide time extensions, under certain conditions, for municipal dischargers, and provide for modified compliance schedules for industry, to meet the first-phase limitations. Secondary treatment requirements may be modified for certain coastal municipalities discharging into deep marine waters. Section 301(b)(1)(C) provides for more stringent limitations when the application of secondary treatment by publicly-owned treatment works (POTW's) or best practical control technology by non-POTW's will not achieve compliance with water quality standards.

The amendments provide three classes of pollutants for the next phase of cleanup: toxic, conventional and non-conventional. For the 65 chemicals listed as toxic in the settlement agreement, industry must comply with effluent limitations requiring application of "best available technology" (BAT) by July 1, 1984. If EPA sets a toxic standard [under Section 307(a)] instead of BAT, industry must comply within 1-3 years after the toxic standard is set.

For any chemical added to the toxic list, EPA must promulgate BAT regulations as soon as practicable. In-



Harold T. Johnson (D-Calif.) comments . . .

Early last year when the House Committee on Public Works and Transportation, of which I am chairman, began to outline its legislative agenda for this session of Congress, one of the areas under discussion was toxic substances in the environment. The Committee carefully reviewed the complex interrelationship of federal statutes dealing with various aspects of toxic substance control.

Because of the importance of controlling these substances, our Subcommittee on Investigations and Review conducted a thorough review of the portion of the program contained in the Federal Water Pollution Control Act Amendments of 1972, P.L. 92-500. At the same time, I asked the Committee staff to prepare a summary of the federal statutory authorities for the control of toxic substances. This paper was prepared by Bruce Barrett of the Dept. of Commerce who worked with the Committee under the Dept. of Commerce's Science and Technology Fellowship program. Barrett's paper is an excellent summary of the many laws that control toxic substances in the aquatic environment.

Industry must comply with BAT not later than 3 years after the standard is set. If EPA sets a toxic standard instead of BAT, industry must comply within 1-3 years after the standard is set.

EPA must identify conventional pollutants (BOD or suspended solids) and set effluent limitations requiring "best conventional pollutant control technology." Industry must comply by July 1, 1984. This level of technology can be no less than BPT, and as high as BAT.

For all unconventional pollutants (pollutants other than toxic or conventional) industry must comply with BAT, subject to stringent waiver requirements, no later than July 1, 1987.

Section 302, Water Quality Related Effluent Limitations, states that in those situations where the application of best available technology effluent limitations required by Section 301(b)(2) would not attain or maintain water quality goals, more stringent limitations must be imposed to attain these goals.

Section 306, National Standards of Performance, provides for the development of standards of performance for new point-source discharges, based on control technology, processes, operating methods, or other alternatives.

Sections 307(b) and (c), Pretreatment Standards, requires that such standards for discharges of pollutants

(including toxic substances) into publicly-owned treatment works be promulgated. Such standards must prevent the discharge of any pollutant into publicly-owned treatment works that would interfere with, or otherwise be incompatible with such works.

The amendments provide that pretreatment requirements for toxic pollutants may be revised by the locality, under certain conditions, where the municipal treatment works removes all or part of the toxic pollutants.

Section 402, National Pollutant Discharge Elimination Systems (NPDES), requires that a permit from EPA or a state with an EPA-approved permit program be issued for the discharge of pollutants from a point-source into navigable waters. The permit may be issued for up to a five-year period, and must require compliance with all applicable requirements under sections 301, 302, 306, 307, 308, and 403.

Section 403, Ocean Discharge Criteria, states that the administrator must develop guidelines for determining the degradation of the waters of the territorial seas, the contiguous zone, and the oceans, which shall include effects on human health and welfare, on marine life, and on esthetic, recreation, and economic values. Section 402 permits must be in compliance with such guidelines.

Section 404, Disposal of Dredged and Fill Material, requires that a permit be issued by the Army Corps of Engineers for the discharge of dredged or fill material into navigable waters at specified disposal sites. The EPA administrator may prohibit the use of any disposal site should he find that the disposal of dredged or fill material will have unacceptably adverse effects on a water use at that site. For those dredging projects where the dredged material contains toxic materials and for which there is no discharge to navigable waters, Section 10 of the Rivers and Harbors Act of 1899 may still be used to evaluate these toxic materials, and the most environmentally acceptable place for disposal.

The recent amendments clarify the extent of the Corps of Engineers authority; specifically exempt certain farming, ranching, and forestry activities; authorize general permits on a statewide, regional or national basis; and provide for exercise of state regulatory authority over certain waters.

Certain federal projects specifically authorized by Congress on an individual basis would be exempt from Corps or state permit authority provided the impact of dredge and fill activities involved had been evaluated in an environmental impact statement.

These exemptions do not apply to discharges of dredge and fill material containing toxic pollutants regulated under section 307(a).

Section 405, Disposal of Sewage Sludge, was amended to require EPA to develop and publish regulations providing guidelines for the disposal and the utilization of sludge. Once established, it is unlawful for the owner or operator of a publicly-owned treatment works to dispose of sludge except in accordance with the guidelines. A permit for the discharge of sewage sludge must be issued pursuant to Section 402.

Section 115, In-place Toxic Pollutants, states that the administrator is directed to identify the location of in-place pollutants, with emphasis on toxic pollutants, in harbors and navigable waterways. This section authorizes him, acting through the Secretary of the Army, to let contracts for the removal and disposal of such materials from critical port and harbor areas.

Section 504, Emergency Powers, stipulates that the ad-



plicable discharges as soon as possible but no later than June 30, 1983 or, for new sources, as specified in Sections 306 and 307.

As previously noted, the recent amendments extended the date for achieving BAT, but it is not clear what effect this will have on the dates specified in the settlement agreement.

Water quality criteria [pursuant to Section 304(a)] must be developed for each of the 65 toxic pollutants with recommended maximum permissible concentrations (where appropriate, zero). If effluent limitations and standards developed according to the agreement are inadequate to maintain 1983 water quality goals (that is, fishable-swimmable water) then more stringent limitations and standards must be imposed.

Pretreatment standards analogous to best practicable control technology were developed for the eight industrial categories and were published in the *Federal Register*.

The Settlement Agreement further required 307(a) standards by late 1976 or early 1977 for aldrin/dieldrin, DDT (DDD, DDE), endrin, toxaphene, benzidine, and PCBs. Such standards have been promulgated.

The FWPCA provides no explicit control mechanisms for toxic pollutants from nonpoint sources. Section 208 requires planning for the control of nonpoint source pollutants, but does not provide controls, other than those controls that may be developed by state and local authorities as part of a 208 plan.

administrator may bring suit to immediately stop the discharge of pollutants, or take other action as may be necessary, when he finds that such pollutants present an imminent and substantial endangerment to human health and welfare. The recent amendments establish a \$10 million contingency fund to be used by EPA to provide emergency assistance to victims of spills or discharges that pose an immediate and substantial risk to public health and welfare or the environment.

The Settlement Agreement, the resolution to four lawsuits brought by environmental groups (against the EPA) seeking the establishment of effluent limitations, pretreatment standards, and toxic pollutant standards, was adopted by the court as a consent decree, which requires EPA to develop:

- best available technology effluent limitations and guidelines

- new source performance standards
- pretreatment standards

for 21 specified industrial categories.

The limitations and standards must be expressly applicable to each of a list of 65 toxic pollutants (elements, compounds, or families of compounds), except that the administrator may exclude one or more of these pollutants if other sections [for example, 301, 304, 306, 307(a), 307(b), or 307(c)] already provide adequate protection, or if a pollutant is present in insignificant amounts. Categories of sources may be excluded from pretreatment standards if they discharge only pollutants treatable by POTW's or if toxic substances are present in insignificant amounts.

The limitations and standards must cover at least 95% of all sources within each industrial category or, for pretreatment, 95% of the sources or 95% of the pollutants discharged by a category. Final regulations are due between March 31, 1979 and December 31, 1979 on an explicit schedule.

The limitations and standards must be achieved by ap-

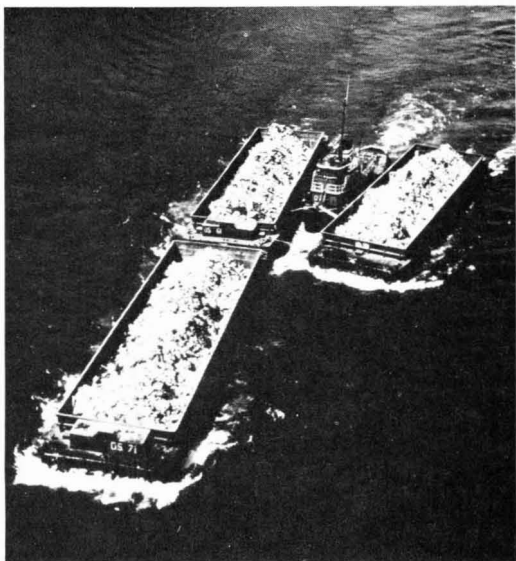
Marine protection, research, and sanctuaries act of 1972

This act, sometimes referred to as the Ocean Dumping Act, controls the dumping of materials, including toxic substances, into the oceans

The act declares that it is the policy of the U.S. to regulate the ocean dumping of materials that adversely affect human health and welfare. "Material" is defined as matter of any kind, including radioactive materials, but does not mean oil within the meaning of Section 311 of the FWPCA or sewage from vessels within the meaning of Section 312 of the FWPCA. "Dumping" means the deposition of material, but does not mean effluents regulated by the FWPCA, Section 13 of the Rivers and Harbors Act of 1899, or the Atomic Energy Act.

This act stipulates that no person may transport for the purpose of ocean dumping, or dump into the ocean, any radiological, chemical, or biological warfare agent or any high-level radioactive waste or, except as authorized by a permit, any other material. The EPA administrator may issue permits for the transportation and dumping of materials (other than radiological, chemical, and biological warfare agents, and dredged material) should he determine that such dumping will not unreasonably degrade or endanger human health or welfare.

It should be pointed out that several permit holders have



Safe drinking water act of 1974

This act requires EPA to establish regulations for drinking water applicable to public water systems

Such regulations include: primary (health-related) drinking water regulations setting forth maximum contaminant levels in water that is delivered to any user of a public water system; and secondary (welfare-related) drinking water regulations controlling odor, appearance, and other contaminants that may adversely affect the public welfare.

These regulations apply to water *after* treatment, as it is delivered to customers, not to water in streams or lakes, and thus do not overlap with authorities granted in other statutes under discussion. The act gives to the states primary enforcement responsibility. If the states fail to act, EPA must assume this responsibility, but may only do so for the primary drinking water regulations.

The act gives the administrator emergency powers to take such action as he deems necessary when he finds that drinking water contaminants present an imminent and substantial endangerment to human health, and the appropriate state and local officials have not acted to protect the health of their constituencies.

In order to provide protection of underground sources of drinking water, EPA must develop regulations for state underground injection control programs. Each state, for which EPA deems such a program a necessity, must then make application to EPA for approval of its state program.

EPA anticipates that eventually all states will need such programs. Initially, however, EPA intends to designate about 18 states, although others may request such designation. Many states already have some type of control

been dumping sludge into the oceans that contain heavy metals in excess of the concentration levels established by EPA. These permit holders are allowed to continue this practice primarily because there currently are no available, economically feasible disposal alternatives.

The Secretary of the Army (Corps of Engineers) may issue permits for the transportation of dredged material for the purpose of ocean dumping should he determine that such dumping will not unreasonably degrade or endanger human health or welfare. All licenses and permits issued pursuant to laws other than this act and the 1899 River and Harbor Act are void to the extent they authorize activities regulated by this act.

There is an overlap between this act and Section 404 of the FWPCA. The Army Corps of Engineers has made an administrative determination (with the concurrence of EPA) that dredging operations using pipelines to discharge into the territorial seas (3 miles out) require a permit under Section 404 of the FWPCA (but not a permit under this act), while dredging operations that utilize a vessel to transport and dump the dredged material into the territorial seas or the oceans require a permit under Section 103 of this act, but not a Section 404 permit. They have not been challenged on this administrative determination.

EPA has made a similar determination that materials discharged by pipeline to the territorial seas or the oceans require a permit under Section 402 of the FWPCA, but not a permit under this act. However, materials transported and dumped by vessels require a permit under this act, but not a Section 402 permit.

It should be noted that the U.S. is a signatory to the Convention on the Prevention of Marine Pollution by Dumping of Waters and Other Matter, adopted by the U.S. pursuant to P.L. 93-254, and made effective in the U.S. on August 30, 1975. This convention sets forth certain standards and criteria for the dumping of materials into the oceans that are binding on the U.S. and other signatories to the convention. Under the convention, nations agree to regulate and require permits for ocean dumping through national administrative authorities, which in the case of the U.S. is P.L. 92-532, the Marine Protection, Research, and Sanctuaries Act.



program, but because the EPA regulations have not been finalized, it has not been determined how many states will qualify.

State programs must: include a requirement that underground injection of fluids is prohibited unless authorized by permit or rule by the state; require that underground injection of fluids will not endanger drinking water sources; and include inspection, monitoring, recordkeeping, and reporting requirements. There may not be requirements that interfere with or impede the underground injection of brine or other fluids that are brought to the surface in connection with oil or natural gas production or any underground injection for the secondary or tertiary recovery of oil or natural gas unless such requirements are essential to assure that underground sources of drinking water will not be endangered by such injections. The states have primary enforcement responsibility. If a state fails to develop and enforce an adequate program, EPA must assume this responsibility.

The underground injection control program regulations will not initially cover pits, ponds and lagoons, which can be sources of groundwater pollution. Regulation of such sources could potentially conflict with the recommended treatment technologies contained in the effluent guideline regulations of P.L. 92-500.

Resource conservation and recovery act of 1976

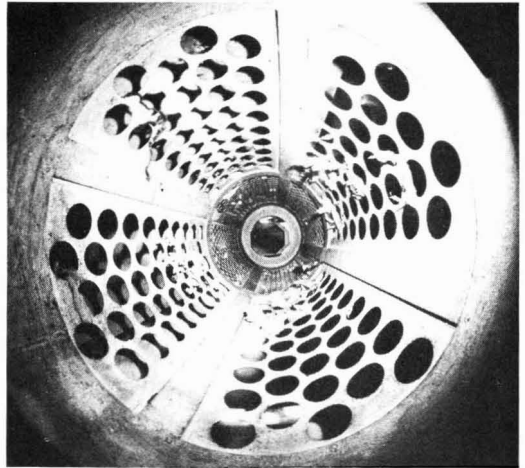
This act controls water pollution indirectly by requiring a regulatory system for the treatment, storage, and disposal of hazardous wastes

The environmentally sound handling of hazardous wastes by generators, transporters and owners and operators of disposal facilities lessens the chance that such wastes will enter the water environment.

This act defines solid waste as any discarded material (including sludge) resulting from industrial, commercial, mining, and agricultural operations, and from community activities. This does not include solid or dissolved material in wastewater discharges that are point sources and are subject to NPDES permits, or nuclear wastes subject to the Atomic Energy Act. Hazardous waste is a solid waste that, because of its quantity or characteristics, may be hazardous to human health or to the environment.

Although not mandated in the act, the administrator could promulgate regulations that would require that all handlers of hazardous waste notify EPA of their activities. Subtitle C of the act, Hazardous Waste Management, requires the EPA administrator to:

- develop and promulgate criteria for identifying the characteristics of hazardous waste, and for listing hazardous waste
- promulgate regulations that identify the characteristics of hazardous waste, and list particular hazardous wastes
- promulgate standards applicable to generators of hazardous waste as necessary to protect human health and the environment that require recordkeeping practices, la-



belonging practices, use of appropriate containers, furnishing information on chemical compositions, use of a manifest system, and submission of reports

- promulgate regulations applicable to transporters of hazardous wastes that require recordkeeping, transportation of only properly labeled hazardous wastes, compliance with the manifest system, and transportation of hazardous wastes only to permitted treatment, storage, or disposal facilities

- promulgate regulations applicable to owners and operators of facilities for the treatment, storage, or disposal of hazardous waste that include requirements for recordkeeping, reporting, monitoring, and inspection and compliance with the manifest system; treatment, storage, and disposal of wastes by satisfactory methods, techniques, and practices; location, design, and construction; contingency plans; maintenance and operation; and compliance with requirements for permits

- promulgate regulations requiring each person owning or operating a facility for the treatment, storage or disposal of identified or listed hazardous wastes to have a permit

- promulgate guidelines to assist states in the development of state hazardous waste programs. State programs, in order to be authorized by EPA, must fulfill these criteria: consistency, equivalency, and adequacy of enforcement.

This act requires that regulations developed by EPA applicable to transporters of hazardous wastes subject to the Hazardous Materials Transportation Act be consistent with the requirements of the latter act. The EPA administrator is authorized to make recommendations to the Secretary of Transportation concerning the regulations of such hazardous waste under the Hazardous Materials Transportation Act for the addition of materials to be covered by that act.

This act does not apply to any activity or substance covered by FWPCA, the Safe Drinking Water Act, the Marine Protection, Research, and Sanctuaries Act, or the Atomic Energy Act except to the extent that such application is not inconsistent with the requirements of these acts.

EPA must integrate all provisions of this act for purposes of administration and enforcement and must avoid duplication (where practicable) with the Clean Air Act, the FWPCA, the Federal Insecticide, Fungicide, and Rodenticide Act, the Safe Drinking Water Act, the Marine Protection, Research, and Sanctuaries Act, and other acts that grant regulatory authority to EPA.

Hazardous materials transportation act of 1974

This act regulates the transportation in commerce of hazardous materials by all transportation modes

When the Secretary of Transportation finds that the transportation of a particular quantity and form of material in commerce may pose an unreasonable risk to health and safety or property, he must designate such quantity and form of material or group or class of such materials as a hazardous material. Such materials may include explosives, radioactive materials, etiologic (disease-causing) agents, flammable liquids or solids, combustible liquids or solids, poisons, oxidizing or corrosive materials, and compressed gases.

The secretary may issue regulations for the safe transportation in commerce of hazardous materials. Such regulations apply to persons offering hazardous materials for transportation in commerce, to persons manufacturing hazardous materials containers for use in commerce, and to persons transporting such materials in commerce.



However, the Coast Guard regulates the bulk transportation of hazardous materials in the marine mode under other statutory authorities.

While the regulations primarily deal with immediate transportation hazards such as flammability or toxicity, pollution control is a potential factor in their development. The secretary is authorized to establish criteria for the handling of hazardous materials including the required numbers of personnel; qualifications and training of personnel; inspections; control, detection, and warning equipment; specifications regarding the use of equipment and facilities; and monitoring safety assurance procedures.

Each person who transports hazardous materials in commerce, or who handles containers used for the transportation of these materials may be required to register with the secretary. No person required to register may transport, or handle, containers intended for the transportation of

hazardous materials unless he has on file a registration statement.

Exemptions from the law or regulations may be granted if a person transports hazardous materials in such a manner as to achieve a level of safety that equals or exceeds that which would be required in the absence of such exemption or which would be consistent with the public interest, and the policy of the act in the event there is no existing level of safety established.

The act requires the secretary to issue regulations that prohibit the transportation of radioactive materials on passenger-carrying aircraft in air commerce unless such radioactive materials are used for research or medical diagnosis or treatment and do not pose an unreasonable risk to health and safety.

This act does not cover pipelines that are subject to the Natural Gas Pipeline Safety Act of 1968 or Chapter 30 of Title 18, U.S.C.

Federal insecticide, fungicide, and rodenticide act of 1972

FIFRA helps to control the entry of pesticides into the water environment

All pesticides used in the U.S. must be registered with and classified by EPA. To be classified for general use, EPA must determine that a pesticide product, when used in accordance with commonly recognized practice, will not generally cause unreasonably adverse effects on the environment.

A pesticide will be classified for restricted use if EPA determines that, when used for its registered purpose, a



pesticide product may cause unreasonably adverse effects on the environment, including injury to the applicator. These pesticides will be subject to such restrictions as EPA may impose by regulation.

The EPA administrator has established guidelines specifying the type of data required for support of registrations. Such data include the composition, degradability, use patterns, and chemical/physical properties of the pesticide as these relate on man and his environment.

It is unlawful to use any registered pesticide in a manner inconsistent with its labeling, or to use restricted pesticides for uses other than those for which it is classified.

EPA must establish procedures and regulations for the disposal or storage of pesticide containers and excess amounts of pesticides, and provide for the safe disposal of pesticides for which registrations are canceled.

Section 20 of the act directs the administrator to undertake monitoring activities in water.

Ports and waterways safety act of 1972

The Coast Guard regulates the bulk shipment of oil and hazardous materials by water under authority of this act (PWSA), the Tanker Act, and the Dangerous Cargo Act

Under Title II of the PWSA, the Secretary of the Department of Transportation under which the Coast Guard operates must establish rules and regulations relating to, among other things, the prevention or mitigation of damage to the marine environment, applicable to vessels that carry liquid cargo that is flammable or combustible, oil, or a hazardous polluting substance as designated under the FWPCA. These rules and regulations set forth comprehensive minimum standards of design, construction, alteration, repair, maintenance, and operation of such vessels.



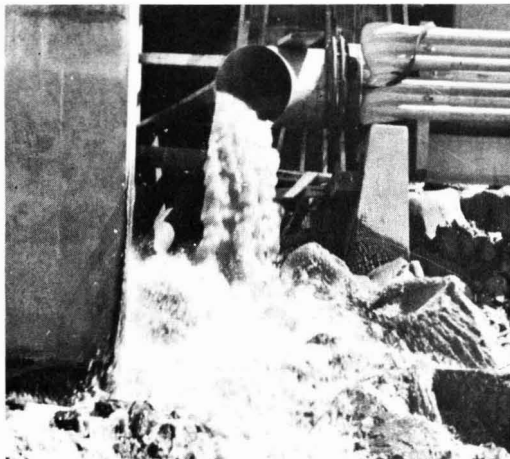
Toxic substances control act of 1976

TSCA gives the EPA broad discretionary authority to control chemical substances that pose an unreasonable risk of injury to health or the environment

The term "chemical substance" is broadly defined to include "any organic or inorganic substance of a particular molecular identity . . ." The term "mixture" used in the law is defined as a combination of chemical substances that is not the result of a chemical reaction. Excluded from the purview of the act are pesticides, foods, drugs, cosmetics, tobacco, liquor and several additional categories of chemicals regulated under other federal laws.

The regulatory approach of TSCA provides for direct control of new and existing chemicals, requires premarket screening of new chemicals, and provides for authority to require the testing of a chemical to determine the extent of the toxicity.

Whenever the EPA administrator makes a finding that there is a reasonable basis to conclude that a chemical substance or mixture poses an unreasonable risk, he must



control that substance or mixture by means of administrative rulemaking. The rules may take a variety of forms, depending on the facts of each particular case.

The administrator may prohibit or limit the manufacture, processing, distribution in commerce, commercial use and/or disposal of a chemical substance or mixture. He may impose labeling requirements, require manufacturers and processors to submit records of their processes and require manufacturers and processors to give notice of any unreasonable risk associated with their chemicals through the chain of distribution.

Anyone who intends to manufacture or process a new chemical substance, or an existing chemical substance for a significant new use must first give EPA at least 90 days advance notice of intent. Upon review of such notification, the administrator determines whether or not to impose regulations.

If a new or existing chemical substance, or mixture, poses an imminent hazard to health or the environment, EPA may initiate a civil action in the federal district court to obtain such judicial relief as may be necessary.

The act also provides EPA with authority to require the testing of a chemical substance of mixture to determine the extent of its toxicity. Where the manufacture, processing, distribution in commerce, use of disposal of a chemical substance or mixture may present an unreasonable risk, or where there is insufficient data and testing may develop data from which to make a reasoned evaluation as to the effects on health and the environment, the administrator may require testing to be done by manufacturers and processors of such chemical substance or mixture. The act establishes an interagency committee with responsibility for drawing up a priority list of no more than fifty chemical substances for testing.

The act provides authority for EPA to require record-keeping and reporting by manufacturers and processors covering: the categories of use for each substance or mixture; the amounts produced; by-products resulting from the manufacture, processing, use, or disposal of the material; data on health and environmental effects; the number of people exposed to the substance in the workplace; and the method of disposal of the substance.

The administrator must coordinate actions taken under TSCA with actions taken under other federal laws and with other federal agencies. If risks associated with a chemical substance or mixture can be eliminated or reduced to a sufficient extent by use of such other laws, the administrator should use such laws to protect against risk unless he determines it to be in the public interest to use the authorities under TSCA.

A major significance of TSCA is that it provides authority to develop information on the impact of chemical substances on the water environment, and allows for broad control of chemicals. If adequate controls cannot be developed through the FWPCA or the Safe Drinking Water Act, action may be invoked under the Toxic Substances Control Act.

Atomic energy act of 1954 (as amended)

The Atomic Energy Act regulates the release of radioactive waste into the environment

These wastes can be separated into two main categories:

- Those discharged to the environment as gaseous or liquid effluents, the radioactive content of which must fall within limits established by the Nuclear Regulatory Commission (NRC) pursuant to this act, or by EPA pursuant to the FWPCA, and which must be as low as reasonably achievable. Under the FWPCA, EPA may set limits on radioactive materials such as radium and accelerator-produced isotopes that are not covered by the Atomic Energy Act.
- Wastes not discharged that are of sufficient potential radiological hazard that they require special care. Wastes in this category include, "high-level wastes" and "other than high-level wastes." The latter wastes are generally buried



in accordance with NRC regulations. The Dept. of Energy has the responsibilities for disposing of high-level wastes and the NRC must regulate such disposal. Although no high-level waste has been buried to date, the first disposal site may be in a deep geological stratum with the wastes in solidified form.

The net effect of policies developed by the NRC and EPA pursuant to this act and the Marine Protection, Research, and Sanctuaries Act has been that no U.S. sea disposal of radioactive wastes has been conducted since 1970.

NRC regulations for the disposal of radioactive wastes relate to discharge into sanitary sewerage systems, burial in soil, and effluents to unrestricted areas. EPA has the authority to establish generally applicable environmental standards for the protection of the general environment from radioactive material.

The FWPCA and the other eight federal acts discussed form the basis for controlling the entrance of toxic pollutants into U.S. waters. These broad authorities offer few loopholes to potential spoilers of this environment.

The author gratefully acknowledges the review efforts and constructive criticisms received from the agencies responsible for implementation of the various statutes discussed in the report. Of special note is the help received from Lester Edelman, Gordon Wood and Bill Corcoran of the staff of the House Committee on Public Works and Transportation.

Additional reading

Federal Environmental Law. Environmental Law Institute, 1974. (Especially the chapter by Robert Zener.)



Bruce R. Barrett is a sanitary engineer in the Office of Environmental Affairs, U.S. Department of Commerce. This paper was prepared during his assignment to the staff of the U.S. House of Representatives' Committee on Public Works and Transportation while a participant in the U.S. Department of Commerce's Science and Technology Fellowship Program.

Regenerative Limestone Slurry Process for Flue Gas Desulfurization

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■ The feasibility of the regenerative limestone slurry process was demonstrated on a bench scale. CaCO_3 and H_2S were recovered from waste sludge from the limestone slurry flue gas desulfurization process. CaCO_3 would be recycled to the scrubber. H_2S would be converted to elemental sulfur in a Claus plant. At 950–980 °C in the presence of coke or coal, 95% of the CaSO_4 and CaSO_3 in the dry sludge was reduced to CaS. The rate-determining reaction was the reduction of CaSO_4 to CaS. The estimated rate constant for this reaction at 850–980 °C was $k \text{ (min}^{-1}\text{)} = 1.7 \times 10^{13} e^{-326/RT}$. At 50 °C, carbonation of an aqueous slurry of the resulting CaS gave more than 98% conversion to CaCO_3 in 35 min. The rate constant for the carbonation at 30–55 °C was $k \text{ (min}^{-1}\text{)} = 8.2 \times 10 e^{-25/RT}$. The overall efficiency of the regeneration was 91–95%. The utilization of successively regenerated limestone was 70% compared to 80% utilization for fresh limestone.

The limestone slurry throwaway process is considered the most advanced for control of SO_2 emissions from power plants (1, 2). Solid waste disposal is still a serious unsolved problem with this process (3). A regenerative process to recover CaCO_3 for reuse and to produce S in a salable form offers a number of advantages over the limestone throwaway process:

- The reuse of CaCO_3 reduces raw material and transportation costs.
- Because the limestone is recycled, only a small amount of makeup limestone is needed. Therefore, capital and operating costs for grinding are reduced significantly.
- Solid waste disposal costs are almost eliminated.
- Holding ponds for waste slurry and regenerated CaCO_3 can be used to maintain a constant production rate in the regeneration plant. There are three significant advantages here: Since CaCO_3 is inexpensive, inventory costs will be low; Ca salts can be stored in solid form, which is more convenient and less costly than storage in the liquid or gaseous forms as in other recovery processes; and if it were advantageous or if the regeneration plant were shut down for any reason, some waste sludge could still be produced for disposal.
- By-product S would be produced for sale.

A thermodynamically favorable route (4) for recovering CaCO_3 for reuse is to convert the S-bearing sludge components to CaS by reductive roasting and then to carbonate the CaS in aqueous slurry using CO_2 from the roasting. The H_2S obtained is an attractive intermediate for the production of elemental S.

The technical feasibility of reductive roasting followed by carbonation has been demonstrated on a bench scale. The chemistry and kinetics of the main reactions have been studied. The efficiency of the various steps in the process and

the effect of regeneration on CaCO_3 reactivity have been estimated.

Experimental

Materials. Materials used were metallurgical coke composed of 1.5% volatile matter, 90% fixed C, 8.5% ash, and 0.74% S; analytical grade CaCO_3 and CaSO_4 ; and CaSO_3 , freshly prepared by saturating an aqueous slurry of CaO with N_2 containing 3% SO_2 . The sample was filtered and dried under an N_2 blanket. The product contained about 6% CaSO_4 compared with >25% in the commercial grade. Dried waste sludge from a pilot plant was used and was composed of 69% CaSO_4 , 8% CaSO_3 , 14% CaCO_3 , and 9% inerts. The CaS samples were either analytical grade or were obtained by thermal decomposition of waste sludge. Commercial grade liquefied CO_2 and N_2 and chemically pure H_2S were used throughout.

Roasting. Two to three grams of presieved, well-mixed coke and CaSO_4 , CaSO_3 , or sludge were heated in a 50 cm^3/min N_2 stream. The samples were removed from the furnace at various time intervals, cooled, and weighed. The residue was analyzed for CaSO_4 and CaSO_3 by conventional gravimetric methods. The gases evolved were analyzed for CO_2 , SO_2 , and H_2S .

Carbonation. To determine the system kinetics, CO_2 in N_2 was bubbled through aqueous CaS slurry contained in a 500-mL glass cylinder in a constant temperature bath. The H_2S produced was collected in 1 N NaOH and analyzed iodometrically. At the end of the run, both the liquid and solid phases in the reactor were analyzed for Ca^{2+} , S^{2-} , CO_3^{2-} , SO_4^{2-} using conventional analytical methods.

To determine the equilibrium, 5 g of CaS in 25 mL water were equilibrated with CO_2 , at pressures ranging from 400 to 760 mm Hg in a 100-mL reaction flask at constant temperature. The slurry was agitated vigorously for about 4 h after which no further change in the composition of the system was observed.

The gas phase was analyzed for H_2S , CO_2 , and H_2O by a gas chromatograph with a thermal conductivity detector. The solid phase was analyzed for CaS and CaCO_3 to ensure that both were present at equilibrium.

Results

Reductive Roasting of Waste Sludge. Decomposition of CaSO_4 . The reductive roasting of CaSO_4 has been studied by several investigators (5, 6). A process that produces H_2SO_4 and cement by calcination with clinker-forming additives developed for general industrial use in Europe (8) has been most widely used (7). Fleck (9) developed and Wheelock et al. (4, 10) reinvestigated a process to produce H_2SO_4 from

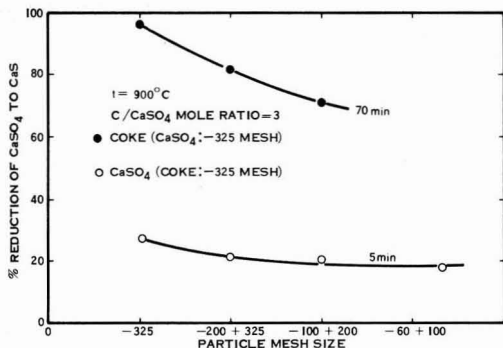
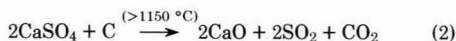
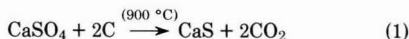


Figure 1. Effect of reactant particle size on rate of reduction of CaSO_4

gypsum, without producing portland cement. Much less effort has been concentrated on the production of CaS from CaSO_4 . A pilot study in India (11) assessed the feasibility of producing S from gypsum. Maximum conversion of gypsum to CaS occurred at about 900°C with coke or lignite as the reducing agent. H_2S was produced from the CaS by 900°C steam.

Two routes may be followed to reduce CaSO_4 . At about 900°C and above 1150°C in the presence of C , the reduction proceeds according to the following reactions:



The effect of experimental variables such as the particle sizes of the CaSO_4 and reducing agent, temperature, and C/CaSO_4 mole ratios on the rate of formation of CaS was assessed to determine the kinetic parameters of the reduction, to optimize CaS production and to minimize CaO and SO_2 formation.

The rate of reduction of CaSO_4 increases as the particle size of the reactants decreases (Figure 1). Increasing the C/CaSO_4 mole ratios also increased the rate of reduction. Beyond a mole ratio of 3, corresponding to 50% excess of the theoretical reductant requirement, no significant increase in reduction rate was observed (Figure 2).

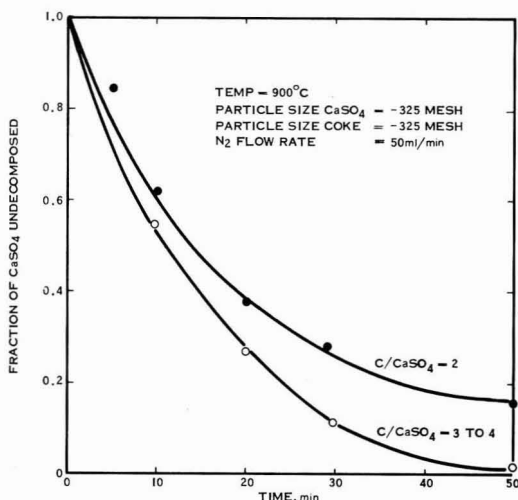


Figure 2. Effect of excess C on rate of reduction of CaSO_4

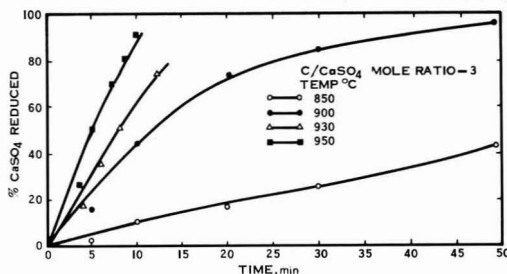


Figure 3. Rate of reduction of CaSO_4 at various temperatures

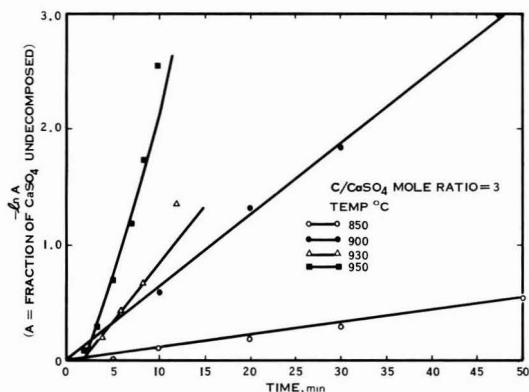


Figure 4. Estimation of rate constant of reduction of CaSO_4 to CaS by C

The rate of CaSO_4 decomposition as a function of time at various temperatures is shown in Figure 3. As expected, the rate increased with increasing temperature.

Plots of $-\ln A$ vs. time are linear for all of the CaSO_4 decomposition rate curves (Figure 4). The rate of decomposition, r , is well represented by the following relation:

$$r = -\frac{dN_{\text{CaSO}_4}}{dt} = kN_{\text{CaSO}_4}$$

the integrated rate equation is

$$-\ln \frac{N_{\text{CaSO}_4}}{N_{\text{CaSO}_{40}}} = -\ln A = kt$$

where N_{CaSO_4} and $N_{\text{CaSO}_{40}}$ are the moles of CaSO_4 in the reactor at time t and time $= 0$, respectively, and $N_{\text{CaSO}_4}/N_{\text{CaSO}_{40}} = A$, is the fraction of undecomposed CaSO_4 .

The estimated rate constants for $850, 900, 930,$ and 950°C are $0.010, 0.061, 0.095,$ and 0.202 min^{-1} , respectively. The temperature dependence of the constant is shown in the Arrhenius plot in Figure 5. In the temperature range of $850\text{--}950^\circ\text{C}$, the rate constant was $k (\text{min}^{-1}) = 1.7 \times 10^{13} e^{-326/R/T}$, and the activation energy was 326 kJ/mol .

Because the production of CaO and SO_2 is also thermodynamically favorable (4), it was expected that some of the CaSO_4 would follow that reaction route. The extent of this side reaction has been assessed at 950 and 980°C and is plotted in Figure 6 as moles of SO_2 released per mole of CaSO_4 . At 950°C about 2% and at 980°C about 8% of the CaSO_4 was converted to CaO and SO_2 within 15 min. The CaO produced is converted to CaCO_3 in the carbonation step.

Decomposition of CaSO_3 . At temperatures above 650°C , CaSO_3 is thermally unstable (12, 13), and three decomposition reactions can occur:

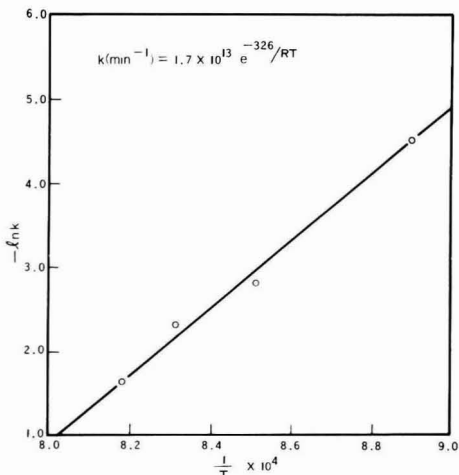


Figure 5. Arrhenius plot: reduction of CaSO_4 to CaS

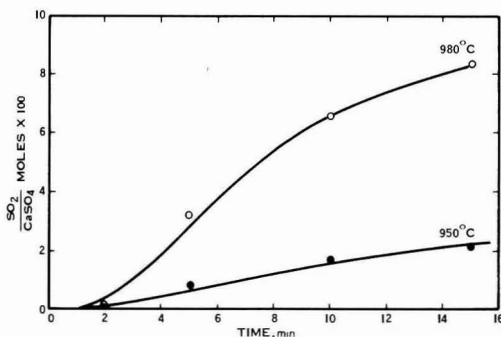
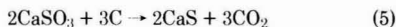
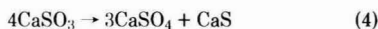
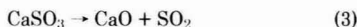


Figure 6. Rate of decomposition of CaSO_4 to CaO



Above 930 °C, within 2 min the CaSO_3 was converted to CaSO_4 , CaS , and CaO . The CaSO_4/CaS ratio of the residue was less than 3, the ratio expected if only disproportionation occurs. Besides the disproportionation and the reduction of CaSO_4 to CaS and CaO , direct reduction of CaSO_3 also takes place. The amount was estimated to be less than 5%. More kinetic data would be required to determine the exact rates of the simultaneous reactions occurring during roasting. For practical purposes, it is adequate to assume a fast, complete conversion of CaSO_3 to CaSO_4 and CaS above 930 °C, and then to consider the rate of formation of CaS and CaO from the CaSO_4 .

Assuming that the rate-determining reaction is the reduction of CaSO_4 to CaS , the sludge decomposition rate curves, the rate of disappearance of the CaSO_4 originally present plus that formed through disproportionation from CaSO_3 , as a function of temperature are shown in Figure 7. The experimental points agree reasonably well with the corresponding estimated values. In about 10 min at 950 and 980 °C, 92 and 90%, respectively, of the CaSO_4 was converted to CaS , and 1.6 and 5.1% was converted to CaO .

Thermal Dissociation of CaCO_3 . In 10 min at 950 and 980

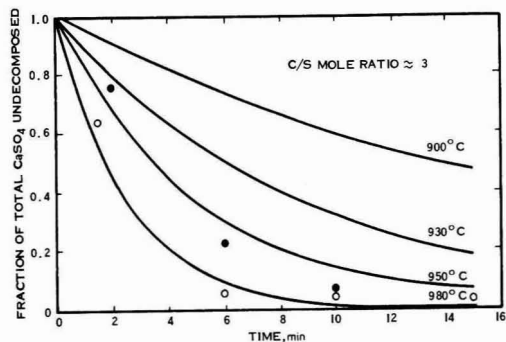


Figure 7. Rate of reduction of CaSO_4 and CaSO_3 in waste sludge to CaS

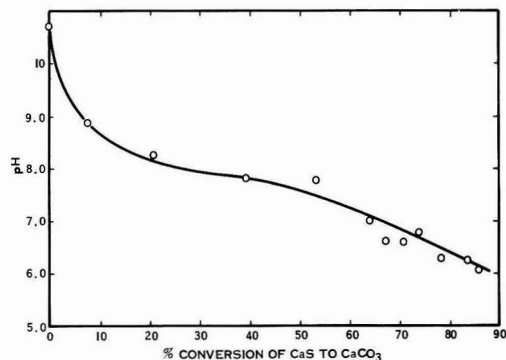
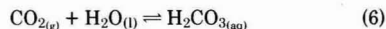


Figure 8. Variation of pH during carbonation

°C, respectively, 97 and 99% of the CaCO_3 dissociate to form CaO and CO_2 .

Carbonation of Aqueous Slurry of CaS . Reactions that may occur during carbonation of an aqueous slurry of CaS are as follows:

CO_2 hydration proceeds through two different mechanisms and rates depending on the system pH (14). Below pH 7, hydration is relatively slow:



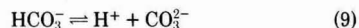
$$k = 0.03 \text{ s}^{-1} \text{ at } 25^\circ\text{C}$$

Above pH 10, CO_2 dissolution is fast:

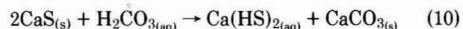


$$k = 8500 \text{ s}^{-1} (\text{mol/l})^{-1}$$

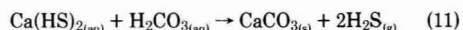
Dissociation of H_2CO_3 and HCO_3^- are fast ionic reactions:



Reaction between CaS and dissolved CO_2 takes place in two stages:



The second step of the carbonation is a fast ionic reaction:



In a well-agitated reactor and with a large excess of CO_2 the liquid film diffusion resistance is minimized, and Reaction 10 is likely to determine the rate.

The experiments were designed to determine the carbonation rate as a function of operating variables. The initial slurry pH of 10.7 decreased to 6 on completion of the carbonation (Figure 8). The carbonation rate as a function of experimental variables is summarized in Figure 9. The CaCO_3 formation rate increased slightly with increasing speed of agitation, as shown in Figure 9A. The maximum agitation speed was used in subsequent runs.

The carbonation rate shown in Figure 9B at four different CaS levels, at otherwise constant experimental conditions, was independent of the CaS content up to a concentration of about 7%. Above this concentration the reaction rate decreased, likely because of difficulty in keeping the solids in suspension.

The carbonation rate increased with increasing CO_2 flow rate (Figure 9C). The optimum CO_2 flow rate with 1 L/min of 12% CO_2 in N_2 was used in all subsequent runs.

Figure 9D shows the carbonation rate increased with increasing temperature. The initial reaction rate appears to be very low. This induction period may be due to an inert layer on the CaS surface. Further investigation is required to understand this phenomenon.

If allowance is made for the induction period, the observed rate curves exhibit a logarithmic relationship between $1 - X_{\text{CaS}}$ and time (Figure 10), $-\ln(1 - X_{\text{CaS}}) = kt$ where X_{CaS}

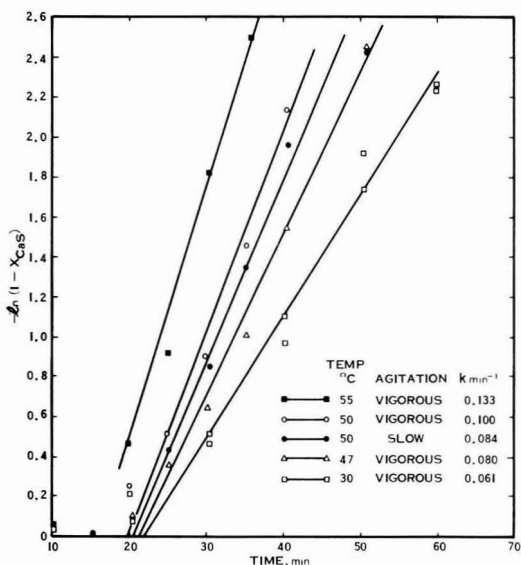


Figure 10. Rate constants of carbonation

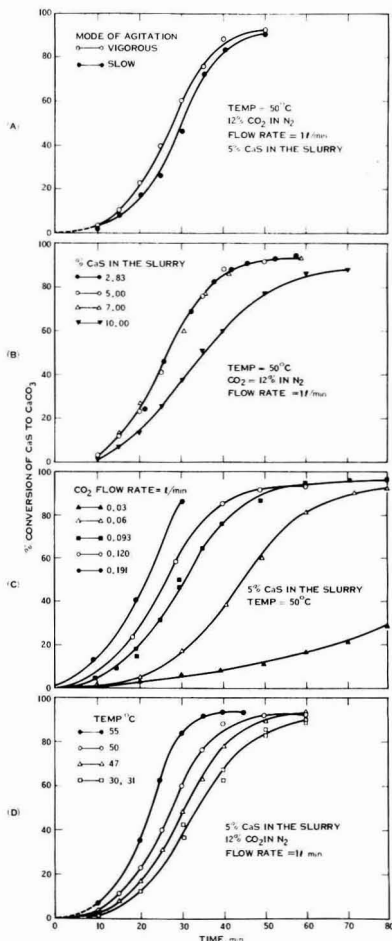


Figure 9. Rate of carbonation as function of: (A) mode of agitation, (B) CaS concentration in slurry, (C) CO_2 flow rate, and (D) temperature

is the fraction of CaS converted to CaCO_3 . The estimated rate constants for the carbonation are 0.061, 0.08, 0.10, and 0.13 at 31, 47, 50, and 55 °C, respectively, disregarding the induction period.

From the shape of the rate curves, it appears that in a well-agitated system in the presence of a large excess of CO_2 , the rate of carbonation is related to the amount of CaS present in the system. The rate decreases as CaS is converted.

Since the reactions occurring during carbonation are heterogeneous reactions involving gaseous, liquid, and solid phases, their progress depends to a great extent on diffusion across the surfaces among the various phases. The rate controlling process in such heterogeneous systems is either diffusion or chemical reaction. The activation energy is often sufficient to distinguish between these two processes. The

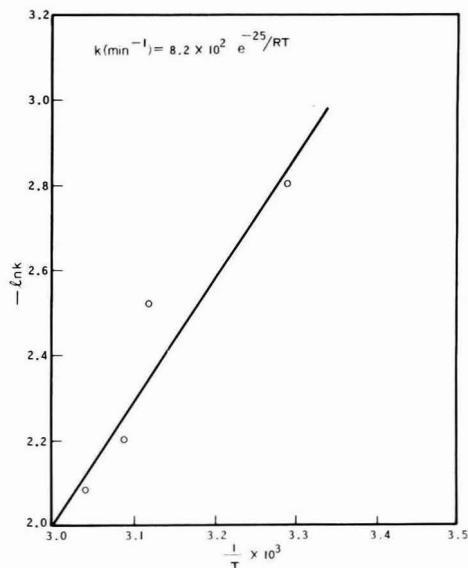


Figure 11. Arrhenius plot: carbonation of CaS

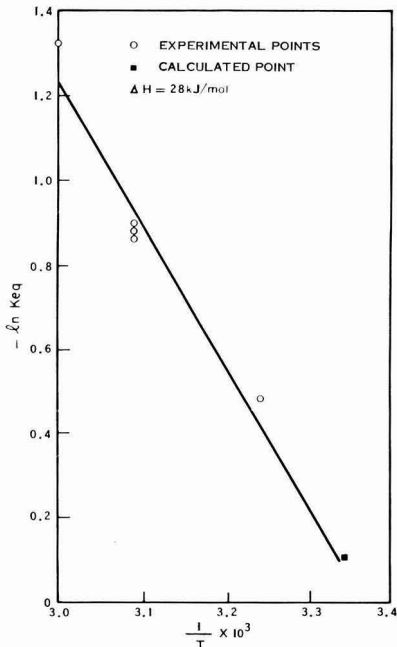
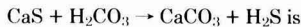


Figure 12. Equilibrium constant of carbonation as function of temperature

temperature dependence of the carbonation rate constants is shown in the Arrhenius plot in Figure 11. In the temperature range of 30–55 °C, the rate constant is k (min^{-1}) = $8.2 \times 10^2 e^{-25/RT}$. The estimated energy of activation is 25 kJ/mol, suggesting diffusion as the rate-controlling process.

The equilibrium constant K_{eq} , of the overall carbonation reaction



$$K_{eq} = \frac{P_{\text{H}_2\text{S}(g)}}{P_{\text{CO}_2(g)}}$$

where $P_{\text{H}_2\text{S}}$ and P_{CO_2} are the partial pressures of H_2S and CO_2 above the system at equilibrium.

Over the temperature range studied, the carbonation was thermodynamically very favorable. In Figure 12 the values of $\ln K_{eq}$ plotted against $1/T$ in K gave a straight line with a slope equal to the heat of carbonation $\Delta H = 28$ kJ/mol. The equilibrium constant estimated from the standard heats of formation agrees well with the experimentally determined values.

At about 50 °C, after 35 min in the carbonator with 12% CO_2 in the carbonating gas, more than 98% of the CaS was converted to CaCO_3 .

Flue Gas Desulfurization with Regenerated CaCO_3 .

A preliminary flow diagram of the proposed regenerative limestone slurry process is shown in Figure 13. To assess the effect of several cycles on the system chemistry, the efficiency of the various process steps, the reactivity of the regenerated carbonate, and the formation of by-products (polythionates and elemental S) with increasing number of regeneration cycles were studied.

The composition of the various streams on three successive regeneration cycles and the efficiencies of the individual regeneration steps are shown in Figure 14. Independent of the number of recyclings, the reductive roasting at 980 °C for 15 min at C/ CaSO_4 and CaSO_3 molar ratios of 2.5 to 3, resulted in a 93–96% conversion of CaSO_4 and CaSO_3 to CaS. The carbonation of CaS with 12% CO_2 in the gas stream resulted in more than 98% conversion of CaS to CaCO_3 . The overall efficiency of the two regenerative steps was between 91 and 95%.

Reactivity of Regenerated CaCO_3 . In Figure 15 SO_2 removal efficiencies are compared using limestone and regenerated CaCO_3 , by plotting removal efficiencies from simulated flue gas against unreacted limestone and regenerated CaCO_3 . The limestone utilization in flue gas desulfurization in the pilot plant was about 80%. After the first recycling, it dropped to 77.5% and decreased further to 72 and 70% in subsequent

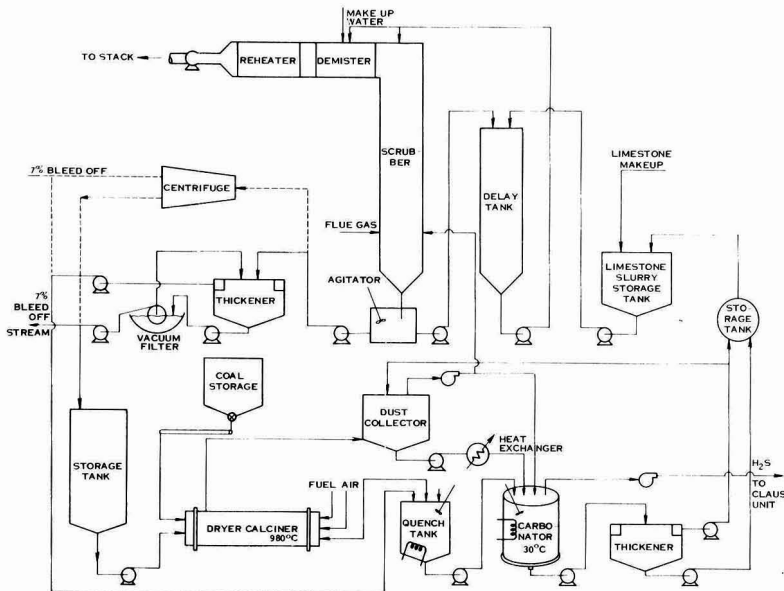


Figure 13. Schematic flow diagram of regenerative limestone slurry process

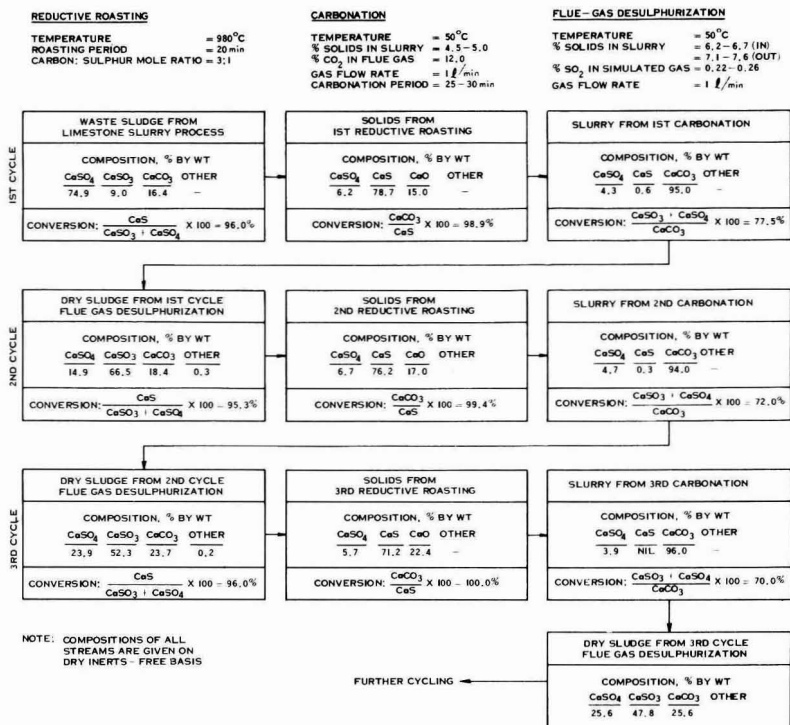


Figure 14. Compositions and efficiencies of individual steps of three successive regeneration cycles

recyclings (Figure 15). Beyond three recyclings the decrease in efficiency was negligible.

Discussion

The technical feasibility of the regenerative limestone slurry process, involving reductive roasting of the waste sludge to CaS, carbonation of the CaS to CaCO₃, then flue gas desulfurization using the regenerated CaCO₃, has been demonstrated on a bench scale.

The rate-determining reaction for roasting the sludge was the reduction of CaSO₄ to CaS. The time required to decompose 95% of the CaSO₄ and CaSO₃ in the sludge at 950-980 °C is about 15 min, using finely ground sludge and coke or coal as C/CaSO₄ mole ratios of about 3. Some CaO is also formed due to the decomposition of CaCO₃ and the reduction of CaSO₄ to CaO. The CaO is converted to CaCO₃ in the carbonation step.

The production of CaCO₃ and H₂S by treating an aqueous slurry of CaS with CO₂ is thermodynamically very favorable. The estimated heat of carbonation in the temperature range of 26-60 °C is 28 kJ/mol. The carbonation rate was a function of the unreacted fraction of CaS in the reacting system. The rate-controlling carbonation step is probably diffusion controlled.

With 35 min residence time in the carbonator, more than 95% of the CaS is converted to CaCO₃ using 12% CO₂ in the carbonating gas. The efficiency of the reductive roasting is 93-96% and of the carbonation is >98%. The utilization of regenerated CaCO₃ in the flue gas desulfurization step decreases from 77 to 72% from the first to the second regeneration cycle, then to 70% in the third. Further decrease is negligible. Overall reagent utilization efficiency in a closed loop operation is 64-66%. The make-up requirement for CaCO₃ was 34-36% of the stoichiometric requirement.

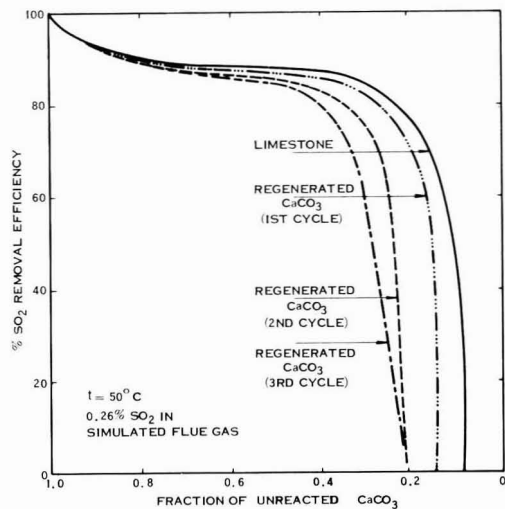


Figure 15. SO₂ removal efficiencies from flue gases by use of aqueous slurries of limestone and regenerated CaCO₃

Coal is as efficient a reductant as coke in the reactions studied, but the amount of CaO produced was higher with coal.

Polythionates are formed during flue gas desulfurization with regenerated CaCO₃ slurries from the reaction between CaS and SO₂ but account for no more than 0.3% of the total S in the system. Polythionates did not accumulate in the system because they were decomposed during roasting.

A feasibility study is recommended to evaluate the applicability of the proposed regeneration system to recover sulfated limestone from the fluidized bed combustion process.

An economic analysis of the regenerative limestone slurry process is required before further development work is undertaken.

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Calibration Factors and Estimation of Atmospheric SO₂ and Fluoride by Use of Solid Absorbents

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■ The use of CaO plates (developed in this work) and PbO₂ plates (after Huey) are discussed as collection media for ambient fluoride and SO₂. The plates provide reliable absorption rates in that the plate surfaces allow for uniform sampling, and quantitative recoveries of absorbed materials are obtained in the extraction processes. Calibration of the plates is effected by referencing the absorption rates against mean ambient concentrations obtained with impinger methods. The resulting calibration factors (for a mean wind speed of 4.7 ± 0.5 miles/h) are 13.9 ± 1.3 and 8.7 ± 1.6 ($\mu\text{g}/\text{m}^3$)/($\mu\text{g}/\text{cm}^2/\text{day}$), respectively, for the PbO₂ and CaO plates. By using these calibration factors it is possible to translate absorption rates into an estimate of the corresponding mean ambient concentrations.

Instrumental methods, including impinger techniques, exist for monitoring atmospheric fluoride and SO₂ (1, 2). Since they are capable of measuring short-term as well as long-term fluctuations, these dynamic techniques are the most desirable. However, they are expensive especially when a large number of stations, such as is necessary for many monitoring programs, are required. In addition, in the case of impinger methods, the level of the impinger solution requires constant attention throughout the sampling period.

Alternate methods, which are inexpensive and require no attention throughout the sampling period, make use of surfaces coated with solid absorbents. Lead dioxide has been used as an absorbent for SO₂, and the most recent modification of this technique has been that introduced by Huey (3). In the Huey procedure a PbO₂ slurry is added to a 48-mm disposable Petri dish and allowed to dry. The prepared plate is then mounted horizontally in a holder and exposed to the ambient

air for a specified period. In the case of fluoride, calcium oxide impregnated on cellulose filters has been used as an absorbent (4). These filters like the candles (5), which preceded the PbO₂ plates, have the disadvantages that a louvered shelter is necessary for their exposure, and shipping procedures are inconvenient and may result in sample loss. For these reasons, we have developed a CaO plate method for fluoride monitoring.

Analysis of the exposed plates will yield absorption rates in units of $\mu\text{g}/\text{cm}^2/\text{day}$. These absorption (or sulfation/fluoridation) rates may be translated into an estimate of the mean ambient concentration for the exposure period by the application of a suitably determined calibration factor. With respect to the PbO₂ plates, calibration factors have evidently not been reported, and in 1969 Huey et al. stated: "The ability of sulfation (rates) to measure SO₂ concentrations remains relatively unknown and will remain so until meaningful instrumental methods are used to measure long-term average (ambient) concentrations" (6). Evidently, the situation described by Huey has remained relatively unchanged in the interim since 1969; in the present work we have used impinger methods to measure long-term ambient concentrations of both SO₂ and fluoride. Comparison of these results with the absorption rates provided by the plates has yielded the required calibration factors.

Since the calibration factors will be dependent upon the absorption rates and these rates in turn will be dependent upon the chemical and physical properties of the absorbing surfaces together with the efficiency of the subsequent extraction of absorbed materials from those surfaces, we have given details regarding both the preparation of the plates and the extraction procedures used. Note that details of the PbO₂ plate preparation and extraction procedures are given because

they vary somewhat from the procedures described by Huey (3).

Experimental

Apparatus. Absorbance measurements for the sulfate test were made at 490 nm with a Unicam SP1700 spectrophotometer and 5.0-cm cells. Calibration was achieved by using Na_2SO_4 standards (see below) over the range 0–40 ppm SO_4 .

For the fluoride test, potential measurements were made with a Fischer Accumet Model 520 digital pH/ion meter equipped with an Orion Model 94-09A fluoride electrode and a calomel reference electrode. Calibration was achieved in the range 0–550 $\mu\text{g F}$ by adding known aliquots of NaF standards (see below) to a representative blank solution.

Reagents. The following reagents were prepared according to the following instructions.

Stock Sulfate Solution (1000 ppm SO_4). Dissolve 1.479 g predried reagent grade Na_2SO_4 in deionized water and dilute to 1 L.

Phosphate Buffer Solution. Dissolve 4.0 g reagent grade $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in deionized water and dilute to 1 L.

PbO_2 Suspension. Add 500 mL 10% ethanol and 5.0 g glass fiber filters to a Waring blender and blend for 1 h. Then add 2.5 g gum tragacanth and 100 g PbO_2 (Hoskins Scientific Ltd., Batch No. 2282-4A). Blend for a further 10 min and then adjust the blending speed so that it is just sufficient to maintain a mixing action.

Stock Fluoride Solution (1000 ppm F). Dissolve 2.210 g predried reagent grade NaF in distilled water and dilute to 1 L.

Acetate Buffer Solution. To 300 mL distilled water add 58 mL glacial acetic acid and 12 g sodium citrate dihydrate. Stir to dissolve and then adjust the pH to 5.2 using 6 N NaOH. Cool and dilute to 1 L.

CaO Suspension. Add 500 mL distilled water and 5.0 g glass fiber filters to a Waring blender and blend for 1 h. Then add 50 g CaO (Fischer, low fluoride). Blend for a further 10 min and then adjust the blending speed so it is just sufficient to maintain a mixing action.

Procedure. The following preparative and analytical steps were followed.

Preparation of PbO_2 Plates. The prepared PbO_2 suspension, 5.0 mL, was added to a 48-mm plastic Petri dish and then allowed to dry over night at 60 °C. Once the prepared plate was dry, a drop of chloroform was added to the center of the plate and pressure was applied. (This step bonds the prepared plate to the Petri dish). Finally, covers were placed on the prepared plates until they were ready to be exposed.

Extraction of PbO_2 Plates. The PbO_2 was quantitatively transferred from the exposed plate to a 250-mL beaker, and

50 mL of the phosphate buffer solution was added. Extraction was achieved by heating at a boiling temperature for 10 min and then allowing to cool to room temperature. The sample was then transferred to a 100-mL volumetric flask, diluted to volume with deionized water, and filtered with Whatman No. 42 filter paper. Finally, a 25-mL aliquot of the filtrate was analyzed for sulfate by a turbidimetric procedure which appears elsewhere (7).

Preparation of CaO Plates. The prepared CaO suspension, 3.5 mL, was added to a 48-mm plastic Petri dish and allowed to dry over night at room temperature. Once the prepared plate was dry, a drop of chloroform was added to the center of the plate and pressure was applied. Finally, covers were placed on the prepared plates until they were ready to be exposed.

Extraction of CaO Plates. The CaO was quantitatively transferred from the exposed plate to a 150-mL polyethylene beaker, and 40 mL distilled water followed by 1.0 mL conc HCl was added. Extraction was achieved by allowing to stand over night. The pH of the extract was then adjusted to pH 5–6 by use of dropwise additions of 6 N HCl or 6 N NaOH as required; Fisher Alkacid test ribbon was used to monitor the adjustment of the pH. Next, 50 mL of the acetate buffer solution was added, and the sample was then transferred to a 100-mL volumetric flask, diluted to volume with distilled water, and then added to a 150-mL polyethylene beaker.

Note that a representative blank was prepared by carrying three blanks through the above procedure, combining them, and then adding a 100-mL aliquot to a 150-mL polyethylene beaker. Data for the standard curves were obtained by using a 0.100-mL Eppendorf pipet and 100 and 1000 ppm F standard solutions to add five successive 10- $\mu\text{g F}$ aliquots followed by five successive 100- $\mu\text{g F}$ aliquots to the prepared blank solution. The cumulative amounts of fluoride added were thus in the range 0–550 $\mu\text{g F}$, and the resulting data allowed for calibration over this range. Details of a similar analytical procedure, including calculation of the blank, which is common to both the calibration solution and the samples, appear elsewhere (8).

Results and Discussion

Absorption Rates for PbO_2 and CaO Plates. Reliable absorption rates will depend on plate surfaces which allow for uniform sampling, and extraction procedures which allow for quantitative recoveries of the absorbed materials. To check for uniform sampling, seven replicate plates were exposed simultaneously to the ambient air for intervals of 14, 21, and 28 days. Table I shows a resulting precision (as a mean relative standard deviation) of 5.2% for the exposed PbO_2 plates. The value of 5.2%, associated with the combined procedure of sampling and analyses, may be compared to the analytical

Table I. Precision and Accuracy for PbO_2 Plates

Sample type	Sample no.	mg SO_4 added ^a	mg SO_4 found ^b	Rel SD, %	Recovery, %
Unexposed plates	S1	0.750	0.743 ± 0.029	3.9	99.1
	S2	1.500	1.473 ± 0.049	3.3	98.2
	S3	3.000	2.934 ± 0.082	2.8	97.8
	Mean			3.3	98.4
Exposed plates	A1		1.110 ± 0.083	7.5	
	A2		1.743 ± 0.066	3.8	
	A3		3.090 ± 0.133	4.3	
	Mean			5.3	

^a The sulfate was added as Na_2SO_4 . ^b The standard deviations are determined from the analyses of seven replicate plates. Samples A1, A2, and A3 were exposed for 14, 21, and 28 days, respectively.

Table II. Precision and Accuracy for CaO Plates

Sample type	Sample no.	$\mu\text{g F added}^a$	$\mu\text{g F found}^b$	Rel SD, %	Recovery, %
Unexposed plates	S1	50.0	49.6 \pm 1.7	3.4	99.1
	S2	100.0	98.9 \pm 2.5	2.5	98.9
	S3	200.0	198.6 \pm 2.6	1.3	99.3
			Mean	2.4	99.1
Exposed plates	A1		32.9 \pm 2.7	8.3	
	A2		56.8 \pm 3.2	5.6	
	A3		110.1 \pm 4.1	3.7	
			Mean	5.9	

^a The fluoride was added as NaF. ^b The standard deviations are determined from the analyses of seven replicate plates. Samples A1, A2, and A3 were exposed for 14, 21, and 28 days, respectively.

precision of 3.3%, obtained when the sulfate is added to the unexposed plates in the laboratory (Table I). The difference between the two values indicates that the plate surfaces generally allow for sampling which is uniform to within approximately 2%. Table II shows the corresponding values for the CaO plates. They are 5.9% for fluoride absorbed as a result of ambient exposure and 2.4% for fluoride added in the laboratory. Again, the small difference in the two values indicates that essentially uniform sampling is provided for by the CaO plates.

Recovery of the absorbed materials has been effected by a Na_3PO_4 extraction in the case of the PbO_2 plates and a HCl extraction in the case of the CaO plates. It has been customary to extract exposed PbO_2 plates with a Na_2CO_3 buffer solution at 100 °C (3). However, difficulty in neutralizing the carbonate prior to the turbidimetric determination has been a serious problem (9). Recently, a Na_3PO_4 buffer solution at 100 °C has been used to extract sulfate from PbO_2 used to recover SO_2 from flue gases (10). The Na_3PO_4 behaves like the Na_2CO_3 in that it provides an alkaline extraction medium (pH \approx 11.5) and, on cooling, preferentially complexes any Pb^{2+} ions, thus leaving the SO_4^{2-} ions in solution. Also, the problems associated with neutralizing the carbonate are, of course, avoided. Reference to Table I shows that the recoveries of sulfate added

to the plates by use of Na_3PO_4 extraction are essentially quantitative, thus indicating an acceptable extraction efficiency; reference to Table II indicates that a corresponding situation exists for the CaO plates. The HCl extraction used in this case is similar to that previously used for lime papers (11).

Calibration of PbO_2 and CaO Plates. The area chosen for the calibration study was in the vicinity of both a lead/zinc smelter and a phosphate fertilizer plant. Both the PbO_2 and CaO plates were calibrated by referencing them against the SO_2 and fluoride collected using an impinger containing 0.1 N NaOH. A Greenburg-Smith standard impinger was used; the flow rate was set at 5 L/min, and the volume of the impinger solution used was 400 mL. Throughout the course of the calibration study, the impinger was run continuously for four successive 7-day sampling periods which commenced at the beginning of each month. The level of the impinger solution was bulked up with distilled water as required. Once returned to the laboratory, the impinger solutions were treated with H_2O_2 , neutralized with 6 N HCl, and then diluted to 500 mL. Separate 25-mL aliquots were then removed, and a turbidimetric analysis for sulfate and a SIE analysis for fluoride were carried out. The analytical procedures used were a variation of the procedures already mentioned and appear in

Table III. Ratios in Units of ($\mu\text{g}/\text{m}^3$)/($\mu\text{g}/\text{cm}^2/\text{Day}$) Used to Determine Calibration Factors for PbO_2 and CaO Plates

Month (1975-76)	No. of days exposure	Mean SO_2 levels		Ratio	Mean F levels		Ratio
		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{cm}^2/\text{day}$		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{cm}^2/\text{day}$	
Sept.	14	141.6	10.62	13.33	1.57	0.221	7.10
	21	132.4	8.23	16.09	1.81	0.180	10.03
	28	123.8	8.62	14.36	1.69	0.193	8.77
Oct.	14	108.8	7.08	15.37	1.53	0.194	7.87
	21	98.6	7.42	13.29	1.36	0.139	9.78
	28	85.6	6.48	13.21	1.35	0.135	10.00
Nov.	14	42.4	3.20	13.25	1.05	0.092	11.41
	21	104.0	6.74	15.43	0.92	0.111	8.29
	28	109.0	7.61	14.32	0.70	0.114	6.14
Dec.	14	93.8	7.13	13.16	0.75	0.103	7.25
	21	99.4	7.42	13.40	0.76	0.095	8.00
	28	110.4	8.55	12.91	1.17	0.104	11.25
Jan.	14	107.8	9.10	11.85	1.51	0.236	6.38
	21	90.2	7.37	12.24	1.37	0.179	7.63
	28	85.4	6.12	13.95	1.32	0.171	7.74
Feb.	14	86.0	6.03	14.26	1.50	0.139	10.82
	21	50.2	3.02	16.62	1.34	0.150	8.93
	28	83.6	6.28	13.31	1.33	0.133	10.00
				Mean ^a 13.91 \pm 1.28			8.74 \pm 1.62

^a The means indicate calibration factors of 13.9 \pm 1.3 and 8.7 \pm 1.6 for the PbO_2 and CaO plates.

detail elsewhere (12). Note that the respective SO₂ and fluoride detection limits for the ambient air are 5 µg SO₂/m³ and 0.1 µg F/m³. The plates were exposed for overlapping time intervals of 14, 21, and 28 days on a monthly basis (Table III). Exposure periods for the plates corresponded to the sampling intervals for two or more successive impinger samples. In this way, average ambient concentrations for varying periods of plate exposure could be calculated by summing and then averaging the appropriate weekly ambient concentrations. In Table III the calculated ambient concentrations together with the corresponding plate results are tabulated. These results yield ratios in units of (µg/m³)/(µg/cm²/day) which are used to compute the calibration factors. The computed factors are 13.9 ± 1.3 and 8.7 ± 1.6 (µg/m³)/(µg/cm²/day), respectively, for the PbO₂ and CaO plates, and they have been determined at a mean wind speed of 4.7 miles/h (see below). The respective relative standard deviations associated with the calibration factors are 9.3 and 18.4%.

In the ideal case where a single gaseous material (at constant ambient concentration and temperature) is being sampled, the theoretical model proposed by Liang et al. (13) indicates that the absorption rate is proportional to the square root of the wind speed. Thus, in the ideal case, the uncertainties in the calibration factors can be attributed to fluctuations in the square root of the wind speed during the sampling period. Analysis of the daily means (14), for the successive 14-, 21- and 28-day sampling periods shown in Table III yielded a mean wind speed of 4.7 ± 0.5 miles/h; the attendant uncertainty associated with the square root of this mean wind speed can be computed to be ±5.5%. Thus, even for ideal situations in the study area, uncertainties of about 5–6% may be expected in the calibration factors, and in real situations even higher uncertainties can be expected. For example, in real situations the following conditions may exist: (i) all the sample may not be present in gaseous form, i.e., aerosols and particulates may be present for which the impinger and plates will exhibit collection capabilities different to those associated with gaseous materials; (ii) more than one gaseous absorbing species may be present, e.g., SO₂ and SO₃ or HF and SiF₄; and (iii) ambient concentrations may be fluctuating during the sampling period. Fluctuations at the emission sources will obviously affect iii, and with respect to iii, note that the presence of certain particulates, aerosols, or gaseous compounds together with fluctuations in meteorological conditions such as sunlight, temperature, humidity, and wind speed will have a complex effect on atmospheric reactions so as to alter the chemical distribution and therefore the concentration levels of gaseous compounds, aerosols, and particulates at the sampling site.

Excluding wind speed, a source of uncertainty in addition to factors i–iii noted above could be fluctuations in meteorological conditions, such as temperature and humidity, at the plate surface. However, since seasonal fluctuations in the calibration factors were not apparent (Table III), it is felt that such fluctuations have a minimal effect on the calibration factors. This observation is in agreement with the findings of previous workers (15, 16). Factors i–iii, then, can be considered to raise the baseline uncertainty from 5.5 to 9.3% for SO₂ and 18.4% for fluoride. Which of the three factors contributes to the much higher uncertainty associated with the CaO calibration factors is not known. However, it seems reasonable to assume that, for the study area, the calibration factors may be used to predict ambient SO₂ levels to within 10% and ambient fluoride levels to within 20%. If we assume that the cumulative effect of the various factors contributing to the uncertainties are not significantly different for other areas, then we can assume that the calibration factors can be generally used to predict ambient levels of both SO₂ and fluoride to within 25%. Note, though, that the calibration factors have

been determined at a mean wind speed of 4.7 ± 0.5 miles/h; if the mean wind speed during the sampling period is known to be significantly different from this value, then according to the model of Liang et al. (13), a correction factor of $(X_1/X_2)^{1/2}$ may be applied where X₁ is the mean wind speed during the sampling period and X₂ is the mean wind speed associated with the calibration factor.

Finally, the calibration factors reported in this work should be used only if the sampling period is at least 7 days or greater. Preliminary results obtained in this laboratory have indicated that the uncertainties associated with the calibration factors increase rapidly as the sampling period decreases from 7 days (17).

Conclusions

Sulfation rates and fluoridation rates together with appropriate calibration factors may generally be used to estimate atmospheric SO₂ and fluoride to within 25%. If the sampling period is 30 days, then the detection limits of 0.1 mg SO₂ and 3.0 µg F associated with the analytical procedures (17) translate into sensitivities of 0.2 µg SO₂/cm²/day and 0.005 µg F/cm²/day. In terms of mean ambient concentrations, for the 30-day period, these values become 3 µg SO₂/m³ and 0.04 µg F/m³. If a 7-day sampling period is considered, the corresponding values are 12 µg SO₂/m³ and 0.2 µg F/m³. The objectives for ambient air quality in British Columbia (18) specify a maximum fluoride level of 1.0 µg F/m³ averaged over 7 days. Thus, a sensitivity corresponding to 0.2 µg F/m³ will allow for a check on compliance with this objective of 1.0 µg F/m³.

The plates are not able to indicate short-term fluctuations in ambient levels of SO₂ and fluoride. However, they are useful for estimating mean ambient concentrations for periods of 7 days or greater and are particularly useful for extensive monitoring programs where only semiquantitative results are required. The results of such a monitoring program for SO₂ in the vicinity of a lead/zinc smelter and for fluoride in the vicinity of an alumina reduction plant are available elsewhere (19). Where comparison data are available, the estimated mean ambient concentrations agree with those obtained using instrumental methods.

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Polynuclear Aromatic Hydrocarbons in Coal—Identification by Their X-ray Excited Optical Luminescence

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■ Several polynuclear aromatic hydrocarbons were isolated from raw coal and detected by their characteristic x-ray excited optical luminescence spectra.

Polynuclear aromatic hydrocarbons (PAH) occur in coal tar pitch (1, 2) in the environment surrounding coke production (3), coal conversion processes, and in coal liquefaction products (4–6). With the exception of 3,4-benzopyrene, which has been measured in various coal dusts (5, 6), very little is known about the occurrence and distribution of PAH's in various coal types. This characterization is a subject of considerable importance because of the carcinogenic nature of many PAH's. With a projected greater utilization of coal as a major source of fuel, the carcinogenic PAH's present in coal may pose a significant occupational health hazard.

Recently, we reported the first observation of x-ray excited sharp-line fluorescence and phosphorescence (XEOL) emitted by a selected group of PAH's present as trace constituents in *n*-heptane, a Shpol'skii solvent (7, 8). Previous studies on PAH's present in environmental samples have utilized high-pressure liquid chromatography or gas chromatography-mass spectroscopy to isolate individual PAH compounds to facilitate their detection and quantification. These analytical techniques are elaborate, time consuming, and require expensive instrumentation. In contrast, the procedure described in this report is less elaborate and is designed to accomplish multicomponent analysis on a sample extract without requiring the time-consuming prior isolation of individual PAH components.

Experimental Facilities and Procedures

Apparatus. The XEOL spectrometric instrumentation has been described (7, 9).

Reagents. All solvents used in this study were of spectra or ACS reagent grade (J. T. Baker Chemical Co. or Fisher Scientific Co.). Benzene was redistilled before use. No luminescence from impurities was detectable in these solvents.

Sephadex LH20 (Sigma Chemical Co.) was washed with a methanol-benzene mixture (1:1) and packed in a column (1.5 cm i.d., 40 cm packed height). The same solvent mixture was used for washing the packed column. Chromatographic grade alumina (60–200 mesh, Matheson Coleman & Bell) and silica

gel (60–200 mesh, grade 950, Baker Chemical Co.) were activated overnight at 240 °C and partially deactivated by the addition of weighed amounts of water to yield a 3% moisture content. The PAH compounds were obtained from Eastman Kodak or Aldrich Chemical Co. and were used without further purification. Coal samples were obtained from the Ames City Power Plant and the Illinois Geological Survey.

Extraction and Isolation of PAH Compounds. A modification of the procedure described by Giger and Blumer (10) was used to separate the PAH's from other compounds that may cause spectral interference or increase the spectral background. The modified procedure provided a relatively pure mixture of PAH's within 30 h in contrast to the 72 h required by the original procedure.

A 15-g coal sample was extracted for 24 h with 150 mL of benzene or cyclohexane in a Soxhlet extractor. The extract was

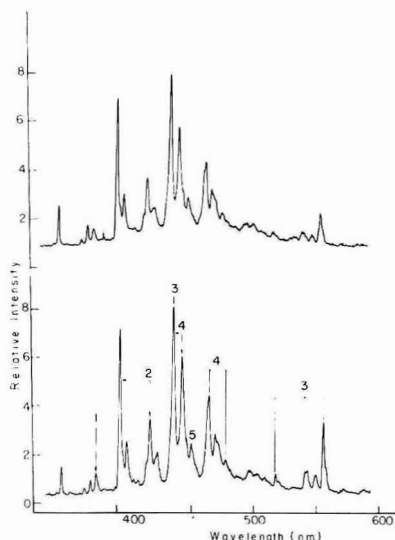


Figure 1. X-ray excited optical luminescence spectra of five PAH's each present at a level of 1 ppm in heptane before (lower) and after (upper) chemical processing of spiked coal samples

1. 1,2-Benzanthracene
2. 3,4-Benzopyrene
3. Coronene
4. Perylene
5. Phenanthrene

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concentrated in a rotary evaporator to a volume of 5 mL, and the concentrate percolated through a column of freshly prepared precipitated copper (1.0 cm i.d. and 20 cm packed height) and eluted with a *n*-heptane-benzene mixture (2:1) to remove elemental sulfur. The solvent in the eluate was evaporated in a rotary evaporator at temperatures <40 °C. The residue, dissolved in 1 mL of methanol, was loaded on a Sephadex LH20 column and the column eluted with a methanol-benzene mixture (1:1) at a flow rate of 0.6 mL/min. The first 55 mL of the brownish-colored eluate was discarded. The next 50-mL eluate containing the PAH fraction was evaporated to dryness in a rotary evaporator at temperatures <40 °C and dissolved in 2 mL of *n*-heptane. The concentrate in *n*-heptane was passed through an alumina-silica gel column (1.2 cm i.d. and 4 cm height each) and eluted with *n*-heptane. The initial 22 mL of *n*-heptane was discarded. The column was next eluted with 20 mL of methylene chloride. The methylene chloride eluate was evaporated to dryness as noted above. This final dried extract was dissolved in a minimum amount of *n*-heptane for analysis by the XEOL technique.

Results and Discussion

Conventional analytical techniques for the detection and quantitation of PAH compounds in environmental samples require isolation of individual compounds present in a mixture (9). In contrast, several PAH compounds present in a mixture can be characterized by the XEOL technique. In the lower half of Figure 1, the composite spectrum of a mixture of 5 PAH compounds in *n*-heptane, each present at the 1 ppm level, is shown. At this level the *S/N* ratio is 40 for perylene in contrast to 5 for 1,2-benzanthracene. (Generally, more than one spectral line may be used to characterize a compound. If spectral overlap occurs, characterization of a compound may be facilitated by obtaining additional information on other emission characteristics of a compound, e.g., thermoluminescence and/or lifetime data (7). The extraction procedures outlined in this communication gave a sufficiently clean sample suitable for the detection of PAH compounds by the XEOL technique. The spectrum shown in the top half of Figure 1 was obtained after the mixture of five PAH compounds was processed through the extraction and column chromatographic separation procedure outlined earlier. The recovery was better than 80% for four of the compounds and about 50% for corone-

ne. For the examination of actual coal samples, the final dried extract was dissolved in 1.0 mL of *n*-heptane, and only 0.2 mL of the solution was used to obtain the XEOL spectra shown in Figure 2. The compounds identified were 1,2-benzanthracene, 3,4-benzopyrene, 3,4,8,9-dibenzopyrene, benzo-*g,h,i*-perylene, perylene, phenanthrene, and 1,2-benzopyrene, most of which are known carcinogenic compounds. The upper spectrum in Figure 2 is representative of PAH compounds present in Iowa coal, and the lower spectrum those present in Illinois coal. The relatively more intense background observed in the spectra in Figure 2 in comparison to those observed in Figure 1 is attributed to the presence of trace level organic impurities in the final extract which have not been characterized. The background emission in Figure 1 is characteristic of the XEOL of *n*-heptane and is probably due to luminescence from chemical species formed during radiolysis of *n*-heptane. If benzene is replaced by cyclohexane in the Soxhlet extraction procedure, much of this background is reduced in intensity.

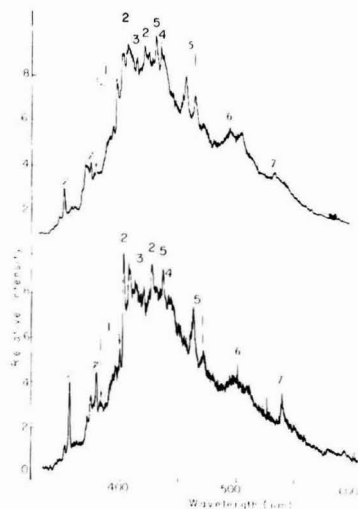


Figure 2. X-ray excited optical luminescence spectra of PAH's isolated from coal samples obtained from Iowa (upper) and Illinois (lower)

1. 1,2-Benzanthracene
2. 3,4-Benzopyrene
3. Benzo-*g,h,i*-perylene
4. 3,4,8,9-Dibenzopyrene
5. Perylene
6. Phenanthrene
7. 1,2-Benzopyrene

The results reported above document the presence of several PAH's other than 3,4-benzopyrene in coal and also demonstrate that the XEOL technique can be used for the simultaneous detection and estimation of a number of PAH compounds in a single extract, without prior isolation of the individual components.

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Reducing Fuel NO_x Emission: N₂ Formation from Fuel N

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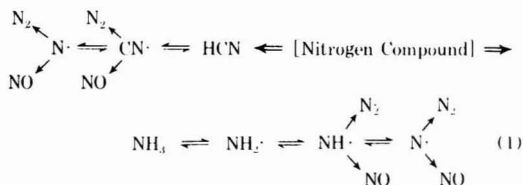
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■ The inert pyrolysis and oxidative pyrolysis of pyridine as a model nitrogen compound were investigated experimentally by means of a tubular flow reactor. The reaction temperatures were varied from 600 to 800 °C. The presence of a small amount of oxygen in a carrier gas enhanced remarkably both the decomposition rate of pyridine and the conversion rate of fuel N into N₂. Inert N₂ for fuel NO_x emission may be formed through a reaction of the type of fuel N → NH₃ → NH₂... → N₂. From the experimental results, a simple model for the conversion of fuel N into N₂ was proposed, and the applicability of the model was verified when the experimental data were satisfactorily compared with the calculated results.

In recent years, nitrogen oxide (NO_x) has surpassed sulfur oxide (SO_x) as a major source of air pollution. Nitrogen oxide from the combustion process is formed from two distinct sources of nitrogen. First, there is nitrogen from the combustion air (thermal NO_x). Second, there is a small amount of bound nitrogen in the fuel (fuel NO_x). Although the importance of reducing total NO_x (=thermal NO_x + fuel NO_x) emission on the basis of the improvement in the combustion technique has been pointed out, an effective combustion method has not been established. This is probably due to the fuel NO_x formation mechanism which has not been made clear yet.

Pershing et al. (1) experimentally separated fuel NO_x from total NO_x and showed that fuel NO_x amounted to the major portion of total NO_x emitted under certain conditions in combustion systems burning both residual oil and pulverized coal with either air or Ar/O₂. Therefore, they emphasized the importance of reducing fuel NO_x emission. On the other hand, the fractional conversion of fuel-bound nitrogen (fuel N) to NO_x has been investigated in various modified combustion systems. For instance, Martin and Berkau (2), Bartok et al. (3), Fenimore (4), and Ogasawara et al. (5) reported the relation between the fractional conversion and the combustion conditions. They have concluded that the fractional conversion of fuel N to NO_x decreases markedly under the condition of fuel-rich combustion and decreases with increased nitrogen concentration in the fuel; further conversion does not appear to be a strong function of compound type.

Sternling and Wendt (6) and Sarofim et al. (7) examined the formation mechanism of fuel NO_x on the basis of previous experimental results and postulated that the fractional conversion of fuel N to NO_x decreases because a part of fuel N may be converted into N₂ through the following intermediates during the pyrolysis of nitrogen compounds.



With attention to these points, Robertus et al. (8) attempted

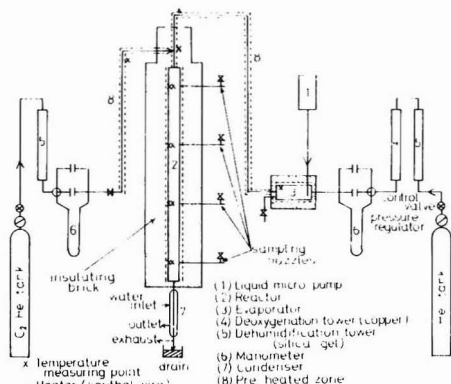


Figure 1. Schematic drawing of experimental apparatus

to eliminate NO_x emission by converting fuel N into N₂ in the pulverized coal furnaces, but could not succeed.

In spite of the importance of the study on the pyrolysis of nitrogen compounds to explain the formation mechanism of fuel NO_x, this subject has been given scant attention. A few papers have been published; for example, Axworthy (9) reported the noncatalytic pyrolysis of pyridine, quinoline, and the like, at some reaction temperature between 900 and 1100 °C. The results showed that fuel NO_x is formed through the HCN route given by Equation 1, but the formation of N₂ was not sufficiently examined.

The objective of this work is to clarify the reducing method of fuel NO_x emission. As a part of the programmed study, the inert pyrolysis and oxidative pyrolysis of nitrogen compounds were investigated experimentally at the reaction temperature below 900 °C, especially, from the viewpoint of making clear both the decomposition rate of nitrogen compound and the conversion rate of fuel N into N₂. The experiments were carried out for pyridine as a model nitrogen compound under the conditions of various reaction temperatures and oxygen concentrations by a tubular flow reactor.

Experimental

Experimental Apparatus and Procedures. A schematic drawing of the experimental apparatus is shown in Figure 1. The reactor used in this study was a tubular flow type. A microfeeder quantitatively supplied the evaporator with liquid nitrogen compound. After mixing the vaporized nitrogen compound with the carrier gas (He) passing through the dehumidification tower, deoxygenation tower (catalyst, pure copper), and orifice meter, the mixture entered into the reactor through the preheated zone. As shown in Figure 1, O₂/He mixing gas could be fed through another flow line; therefore, an arbitrary oxygen concentration was selected at the time of runs. The flow rate of each gas was adjusted with pressure regulators and controlling valves. The reaction tube was a 1/2-in. stainless steel tube (SUS 304TP) 1000 mm long. A Kanthal wire heater (maximum load, 4 kW) was wound around the outside wall of the tube. The reactor was sur-

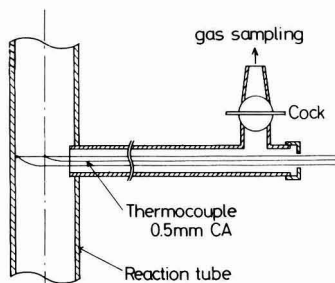


Figure 2. Details of sampling nozzle

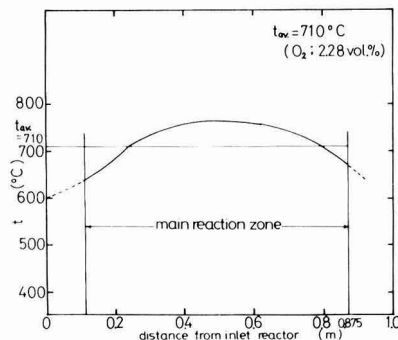


Figure 3. Axial temperature distribution of reactor

Table I. Weight Ratios of H, C, and N in Separated Liquefied Product

	t, °C	C	H	N
Inert	680	75.41	6.97	17.62
pyrolysis,	730	75.97	6.56	17.47
O ₂ = 0%	775	77.13	5.42	17.41
Oxidative	680	75.75	6.63	17.62
pyrolysis,	720	75.55	6.90	17.55
O ₂ = 0.82%	740	75.35	7.28	17.37
	780	75.89	6.68	17.43
Pyridine		75.95	6.33	17.72

rounded with insulating bricks to maintain the axial temperature uniform.

Analyses of Products. As shown in Figure 2, the sampling nozzles were 1/8-in. diam. stainless steel tubes placed at four points along the axial direction of the reactor (125, 375, 625, and 875 mm from the entrance of the reactor). Two thermocouples (Chromel-Alumel with 0.5 mm diam.) were inserted into each sampling nozzle to measure the gas temperatures at both the inside wall and center of the reaction tube. At the exit of the reactor, separation between liquefied and gaseous products was done by a water-cooled condenser. Gaseous and liquefied products were analyzed as follows: for gases, N₂, O₂, CO₂, CO, H₂, and hydrocarbon were measured by gas chromatography, and both NH₃ and HCN were measured by a Kitagawa-Shiki gas detector. A chemiluminescent analyzer was used to measure nitrogen oxide. The weight ratios of H, C, and N in the separated liquefied product were measured by an ultimate analyzer (C.H.N. Corder).

Experimental Conditions. The reaction temperature ranged from 600 to 800 °C. The temperature of the evaporator was maintained continuously at about 350 °C. The oxygen concentration in He was varied from zero to 5% by volume. The dilute mixture proportion of pyridine in He was varied from 0.33 to 0.35 by kg-pyridine/nm³ He. Pyridine as a model nitrogen compound which was used in the present experiment was a pure chemical reagent of highest grade. Then the residue in the reactor was removed completely by burning with heated air (at about 500 °C) at the end of each run.

Results and Discussion

Observed gaseous nitrogen compounds were N₂, NH₃, HCN, and NO; the other gaseous products were CO₂, CO, CH₄, C₃H₈, H₂, O₂, and H₂O. The weight ratios of H, C, and N in the separated liquefied product are listed in Table I. These results were almost equal to weight ratios of H, C, and N in pyridine. An example of the gas temperature distribution in the axial direction is shown in Figure 3. The gas temperature at each point was applied in the arithmetic mean value of the tem-

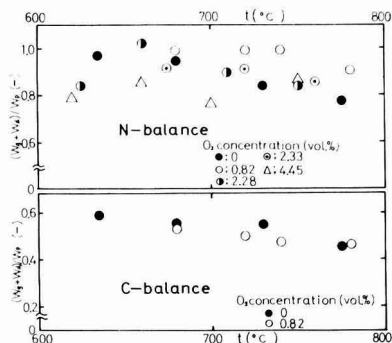


Figure 4. N and C mass balance

peratures measured at the inside wall and the center of the reaction tube where the difference between two temperatures was merely 2 or 3 °C. The reaction temperature of each run was represented by the integral mean value of the temperatures measured between the first and the fourth sampling point. The temperature at each point was maintained constant with the maximum within 5% of the integral mean temperature. The reaction time was estimated on the assumption that gases in the reactor were approximately the mixture of He, O₂, and pyridine vapor, because the oxygen/pyridine ratio was very low at 0.16 (nm³ O₂/kg-pyridine) in comparison with the ratio of 2.05 (nm³ O₂/kg-pyridine) required for the conversion of pyridine into CO₂, NO₂, and H₂O. The mass balances obtained in this experiment are shown in Figure 4. Depending upon the reaction condition from 80 to 100% of the nitrogen was present in the observed products. Similar to Axworthy's results, about half of the carbon could not be detected after the reaction. Possibly, all of the gasified nitrogen was converted into N₂, NH₃, HCN, and NO from Table I and Figure 4 where the concentration of NO is zero in case of O₂ = 0% (inert pyrolysis).

Decomposition Rate of Nitrogen Compound (Pyridine). The fractional decomposition of pyridine may be defined by the following equation as the weight ratio of the gasified nitrogen in the total fuel N fed.

$$a = \left(\frac{x_1 p_1}{14} + \frac{x_2 p_2}{17} + \frac{x_3 p_3}{27} + \frac{x_4 p_4}{30} \right) \left(\frac{79 Q_c}{W_p x_c} \right) \quad (2)$$

The relationships between the fractional decomposition (*a*) and the reaction time (*θ*) are shown in Figure 5 with parameters of the reaction temperature and oxygen concentration. In the case of inert pyrolysis, the proceeding of the decomposition is nearly independent of the reaction temperature in the temperature range of this study (from 600 to 800 °C),

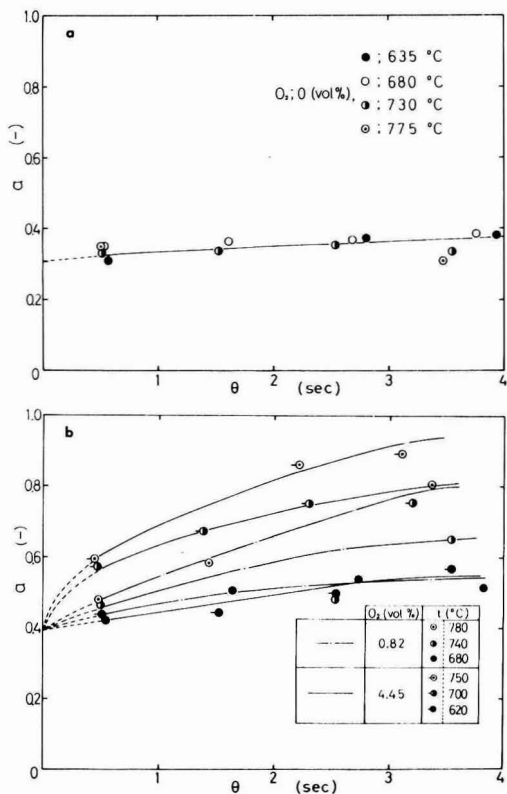


Figure 5. Relation between fractional decomposition (a) and reaction time (θ)

and the fractional decomposition at $\theta = 0$, a_0 , is estimated at about 0.3. Under the presence of oxygen (oxidative pyrolysis) the fractional decomposition increases with an increase in the reaction temperature, and $a_0 = 0.4$ is obtained as shown in Figure 5b. That $a_0 > 0$ at $\theta = 0$ is probably due to the decomposition of a portion of pyridine in between the evaporator and the reactor. That a value of a_0 in the oxidative pyrolysis is larger than that at $O_2 = 0\%$ will be due to injection of oxygen at the upstream point from the entrance of the reactor.

Assuming that the overall decomposition rate can be expressed in the first-order rate equation as follows:

$$\frac{da}{d\theta} = K_1(1 - a) \quad (3)$$

with the initial condition

$$\theta = 0; a = a_0 \quad (4)$$

integrating Equation 3 with the initial condition, we obtain:

$$-\ln \frac{(1 - a)}{(1 - a_0)} = K_1\theta \quad (5)$$

An example of the relation between $-\ln\{(1 - a)/(1 - a_0)\}$ and θ is shown in Figure 6. The proportional relation between the two verified the applicability of Equation 3. Assuming that the decomposition rate constant, K_1 , can be expressed by the following Arrhenius equation:

$$K_1 = A_1 \exp\left(-\frac{E_1}{RT}\right) \quad (6)$$

Both the frequency factor, A_1 , and the activation energy, E_1 ,

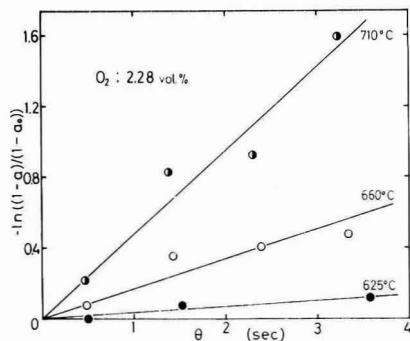


Figure 6. Example of relation between $-\ln\{(1 - a)/(1 - a_0)\}$ and θ

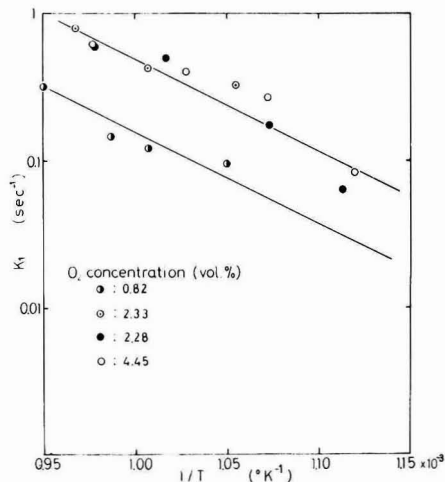


Figure 7. Arrhenius plot for K_1

for the overall decomposition of pyridine were obtained from straight lines shown in Figure 7. The values of A_1 and E_1 at various oxygen concentrations are listed in Table II. In the case of inert pyrolysis in this experimental range, A_1 and E_1 could not be determined because of the dependence of the temperature on K_1 was small. Axworthy measured K_1 at a temperature above 900 °C in the case of inert pyrolysis. The present values obtained in the temperature range of 600–800 °C were considerably different from the values extrapolated by use of Axworthy's data. However, at about 830 °C the results obtained were in close agreement with those obtained by Axworthy. The calculated results of the fractional decomposition obtained by integrating Equation 3 with the measured temperature are plotted with the measured values in Figure 8. Fairly good agreement is shown between calculated and measured results.

Conversion Rate of Fuel N into N_2 . Fractional Conversion of Total Fuel N Fed to Each Gaseous Nitrogen Compound. Fractional conversion, γ , for each component is expressed by the following equations:

$$\begin{aligned} \gamma_{N_2} &= (79/14)(Q_c x_{1\rho_1}/W_p x_c) \\ \gamma_{NH_3} &= (79/17)(Q_c x_{2\rho_2}/W_p x_c) \\ \gamma_{HCN} &= (79/27)(Q_c x_{3\rho_3}/W_p x_c) \\ \gamma_{NO} &= (79/30)(Q_c x_{4\rho_4}/W_p x_c) \end{aligned} \quad (7)$$

$$\gamma_{N_2} + \gamma_{NH_3} + \gamma_{HCN} + \gamma_{NO} = a \quad (8)$$

Table II. A_1 and E_1 at Various Oxygen Concentrations

O ₂ , vol %	A ₁ , 1/s	E ₁ , kcal/mol
0		
0.82	4.0 × 10 ⁵	28.8
2.28	8.4 × 10 ⁵	28.8
2.33	8.4 × 10 ⁵	28.8
4.45	8.4 × 10 ⁵	28.8

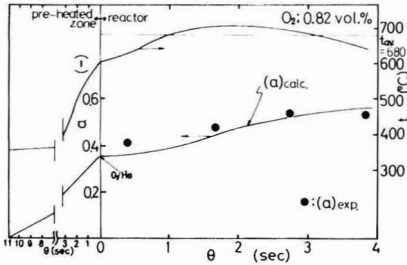


Figure 8. Comparison between calculated results and measured values of fractional decomposition

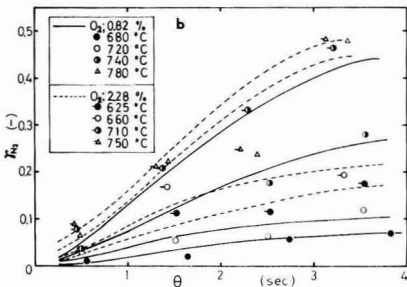
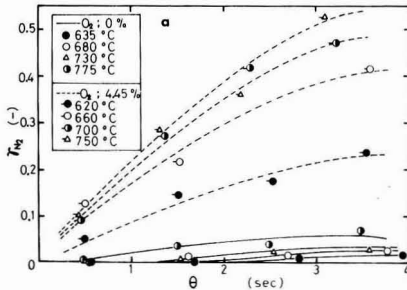


Figure 9. γ_{N_2} vs. θ

To realize the reduction in fuel NO_x emission, it seemed important that the fractional conversion of fuel N to NO and N₂ would be made clear. In the present experiment, however, γ_{NO} was negligibly small in comparison with γ_{N_2} . Therefore, an investigation was made on γ_{N_2} . Figure 9 shows the relation between γ_{N_2} and the reaction time. In general, the values of γ_{N_2} are nearly zero at $\theta = 0$ and also increase with an increase in the oxygen concentration and the reaction time. The comparison between Figure 5 and Figure 9 proves that the time change of γ_{N_2} is not affected much by the decomposition process which occurred in the preheating line.

Fractional Conversion Based on Decomposed Fuel N. The fractional conversion of the decomposed fuel N to each gaseous nitrogen compound, γ' , is defined as follows:

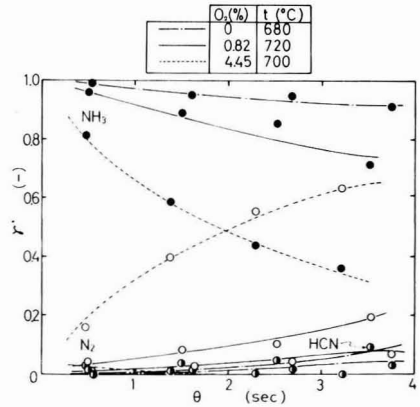


Figure 10. Time change of γ' with parameter of reaction temperature and oxygen concentration

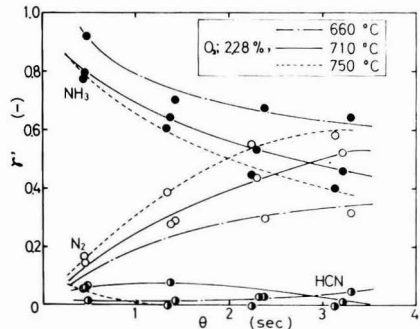


Figure 11. Time change of γ' with parameter of reaction temperature and oxygen concentration

$$\begin{aligned} \gamma'_{N_2} &= \gamma_{N_2}/a, \quad \gamma'_{NH_3} = \gamma_{NH_3}/a \\ \gamma'_{HCN} &= \gamma_{HCN}/a, \quad \gamma'_{NO} = \gamma_{NO}/a \end{aligned} \quad (9)$$

$$\gamma'_{N_2} + \gamma'_{NH_3} + \gamma'_{HCN} + \gamma'_{NO} = 1 \quad (10)$$

Figures 10 and 11 show the time change of γ' with parameters of the reaction temperature and the oxygen concentration. The following results were found from these experiments:

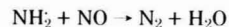
There is a large percentage of NH₃ at the initial period of reaction.

N₂ increases with a decrease in NH₃; especially the value of γ'_{N_2} becomes 0.6 after 3 s under conditions of the reaction temperature and the oxygen concentration of 750 °C and 4.45%, respectively.

The change of HCN with the reaction time is small in comparison with that of N₂ and NH₃.

From these experimental facts, it was suggested that the nitrogen contained within NH₃ converts mainly into N₂.

Thus, a theory that N₂ is formed through the NH₃ route in Equation 1 would be more reliable for the fuel-rich combustion. An example of the time change of NO is shown in Figure 12. It seemed that the rapid decrease in NO was due to some reduction that occurred during the conversion of NH₃ into N₂. As an example, the following reaction could be considered to understand the phenomenon:



Conversion Model and Its Rate Constant. The pyrolysis of this type is a complex reaction mechanism. In this study,

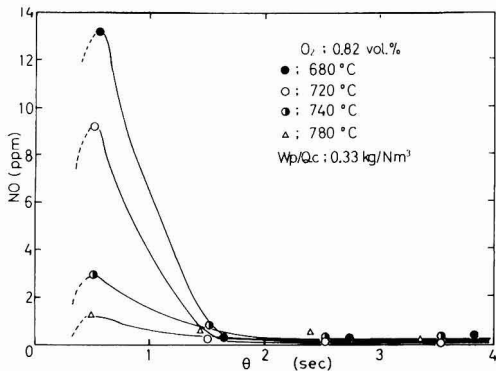


Figure 12. Time change of NO concentration with parameter of reaction temperature

however, first let us assume that the conversion rate of fuel N into N_2 is approximated by the following equations. Provided that its rate is proportional to the product of the fractional undecomposed, $(1 - a)$, and the fractional unconverted, $(1 - \gamma'_{N_2})$, that is,

$$\frac{d\gamma'_{N_2}}{d\theta} = K_2(1 - a)(1 - \gamma'_{N_2}) \quad (11)$$

Integrating Equations 3 and 11 with the initial conditions of $a = a_0$ and $\gamma'_{N_2} = 0$ at $\theta = 0$, we obtain:

$$-\ln(1 - \gamma'_{N_2}) = \left(\frac{K_2}{K_1}\right) (1 - a_0)(1 - e^{-K_1\theta}) \quad (12)$$

Assuming that the relationship between the conversion rate constant, K_2 and the reaction temperature can be expressed by the Arrhenius equation, that is,

$$K_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) \quad (13)$$

In the case where the oxygen concentration is 0.82% by volume, the relationship of $-\ln(1 - \gamma'_{N_2})$ vs. $(1/K_1)(1 - a_0)(1 - e^{-K_1\theta})$ is plotted in Figure 13. From the proportional relation as shown in the figure, the conversion process of fuel N into N_2 was proved well estimable on the basis of Equations 3 and 11. Figure 14 shows the Arrhenius plot for K_2 . Also the values of A_2 and E_2 obtained from the figure are summarized in Table III. Within the present experimental conditions, the effects of the oxygen concentration on A_2 and E_2 are approximately expressed by:

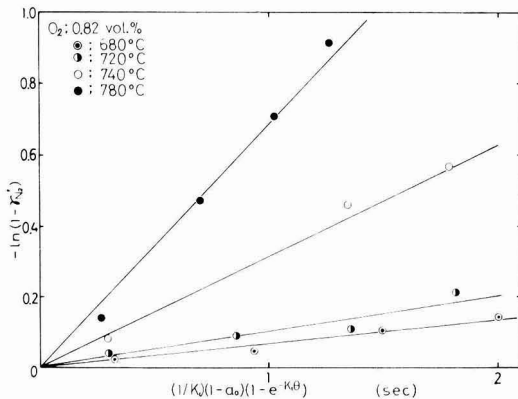


Figure 13. Relation between $-\ln(1 - \gamma'_{N_2})$ and $(1/K_1)(1 - a_0)(1 - e^{-K_1\theta})$

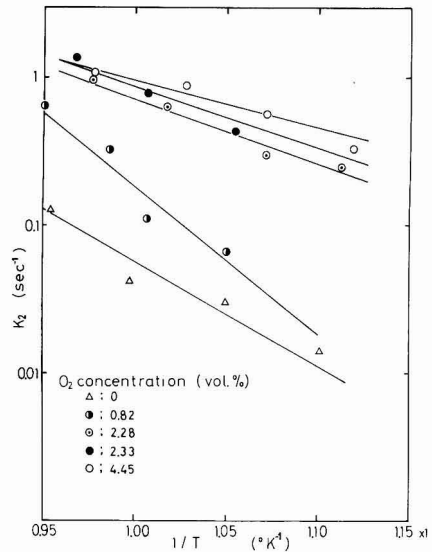


Figure 14. Arrhenius plot for K_2

Table III. A_2 and E_2 at Various Oxygen Concentrations

O ₂ , vol %	A ₂ , 1/s	E ₂ , kcal/mol
0	9.39×10^5	32.7
0.82	1.17×10^9	44.8
2.28	7.63×10^3	18.5
2.33	9.07×10^3	18.4
4.45	1.33×10^3	14.4

$$\ln A_2 = 18.8 - 8.0 \ln [O_2]$$

$$\ln E_2 = 3.55 - 0.64 \ln [O_2] \quad (14)$$

where $[O_2]$ is the oxygen concentration in carrier gas, and its unit is a volumetric percentage.

In the case of inert pyrolysis, however, the values of A_2 and E_2 could not be estimated by Equation 14. Thus, the conversion mechanism of fuel N into N_2 has a typical difference due to the presence or absence of oxygen. Figure 15 shows the comparison of the experimental data, $(\gamma'_{N_2})_{\text{exp}}$ with the calculated results, $(\gamma'_{N_2})_{\text{calc}}$ based on Equations 3, 6, 11, and 13. Furthermore, in the case of inert pyrolysis, $(\gamma'_{N_2})_{\text{calc}}$ calculated using Axworthy's data for K_1 are shown in the same figure. A fairly good agreement between the experimental and the calculated results verified that the conversion process of fuel N into N_2 could satisfactorily be expressed by the proposed simple conversion model.

Provided that the results obtained in this study will be applied to the first stage of multistage combustion, a significant elimination in total NO_x emission from commercial combustion equipment would be achievable.

Conclusion

Both the inert pyrolysis and the oxidative pyrolysis of pyridine as a model nitrogen compound were investigated experimentally to clarify the formation mechanism of fuel NO_x and the combustion technique of reducing total NO_x emission by means of a tubular flow reactor.

The presence of a small amount of oxygen in the carrier gas remarkably enhanced both the decomposition rate of pyridine and the conversion rate of fuel N into N_2 .

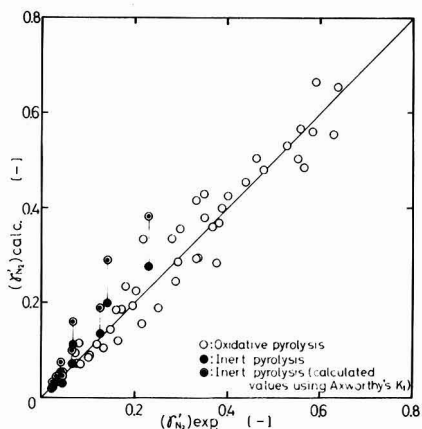


Figure 15. Comparison of experimental data $(\gamma'_{N_2})_{exp}$ with calculated results $(\gamma'_{N_2})_{calc}$ based on Equations 3, 6, 11, and 13

Inert N_2 for fuel NO_x emission is formed through the NH_3 route shown in Equation 1.

The conversion rate of fuel N into N_2 can be approximately expressed in the following equations, and its rate constants K_1 and K_2 are obtained using the experimental data:

$$d\gamma'_{N_2}/d\theta = K_2(1 - a)(1 - \gamma'_{N_2})$$

$$da/d\theta = K_1(1 - a)$$

Acknowledgment

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Nomenclature

a = fractional decomposition of pyridine, -

a_0 = fractional decomposition of pyridine at entrance of reactor, -

A_1, A_2 = frequency factor, 1/h

E_1, E_2 = activation energy, kcal/kmol

K_1, K_2 = rate constant, 1/h

Q = volumetric velocity of gas, m^3/h

R = gas constant, kcal/K-kmol

T, t = reaction temperature, K, °C

W_d = mass velocity of liquefied product, kg/h

W_g = mass velocity of gaseous product, kg/h

W_p = mass velocity of pyridine, kg/h

x = concentration of gaseous product by volume ratio, -

γ = fractional conversion based on total fuel N fed, -

γ' = fractional conversion based on decomposed fuel N, -

θ = reaction time, h

ρ = density, kg/m^3

Subscripts

c = helium (He)

1 = nitrogen (N_2)

2 = ammonia (NH_3)

3 = hydrogen cyanide (HCN)

4 = nitric monoxide (NO)

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Effects of Mn Deposits from MMT on Automotive Catalysts in the Absence and Presence of Other Fuel Additives

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■ The chemical effects of deposits from methylcyclopentadienyl manganese tricarbonyl (MMT) on three-way catalysts were investigated. Automotive exhaust was simulated by the combustion of isooctane. Depending on the experiment, MMT and/or other fuel additives were introduced. Two formulations on monolithic supports did not show any chemical poisoning beyond that caused by the same fuels without MMT. In addition, no effect of MMT on the sulfuric-acid formation over the same catalysts was found. A pronounced catalytic effect of the Mn deposit on the exhaust composition upstream of the catalyst caused a decrease of the NO concentration and an increase of the unburnt hydrocarbons.

The adverse influence of common additives and contaminants in fuel and engine oil, such as Pb, P, S, and halides, on the removal of automotive emissions has been extensively demonstrated (1). Thus, the use of another fuel additive should be viewed with caution since it has to be established that the undesired side effects on regulated emissions (hydrocarbons, CO, and NO) or on the small amounts of unregulated emissions, such as NH₃, SO₃, H₂S, and HCN, do not outweigh the potential benefits. For this reason, the effects of methylcyclopentadienyl manganese tricarbonyl (MMT) should be studied in detail, since this compound is already used in small amounts in several gasolines for adjusting the octane rating.

Earlier Studies

Almost five years ago we investigated chemical poisoning of monolithic oxidation catalysts containing Pt and Pd in exhaust produced by the combustion of isooctane with MMT in the laboratory. Two runs, lasting 30 and 17 h, were carried out at a temperature of 500 °C and a manganese concentration of 0.8 g/gal of isooctane. The combustion, adjusted to simulate automotive exhaust, produced 3.8% CO, about 600 ppm of unburnt hydrocarbons (measured as hexane), 100 ppm NO, and corresponding levels of CO₂ and water. An excess of 4% oxygen was introduced into the exhaust. The MMT produced a finely divided, brownish deposit on the catalyst; however, only a fraction of the deposit was retained permanently after the use of isooctane without MMT. Analysis of the catalyst run for 17 h showed a Mn concentration of only 0.04 wt %. No catalyst deterioration was indicated by measurements of light-off temperature and the platinum-metal surface area.

In another experiment the catalyst was kept in the exhaust for 30 h under similar conditions, but without secondary oxygen. When the light-off temperature was measured, a severe deactivation was noted at first. However, further treatment under oxidizing conditions at 500 °C for half an hour restored the catalyst activity completely.

At that time, no further experiments were carried out, because parallel tests on an engine dynamometer, which was operated under oxidizing conditions, showed severe clogging of the passage channels of a monolithic catalyst by Mn deposits.

As MMT is now added to several gasolines at low levels (below 0.125 g Mn/gal), its effect on present exhaust catalysts

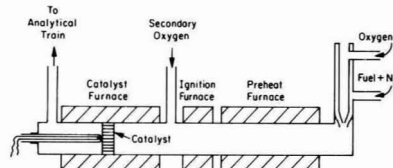


Figure 1. Pulse-flame apparatus

is being investigated by several research groups. In several engine tests no evidence was found for the chemical poisoning of current noble-metal oxidation catalysts by MMT (2-7), in agreement with our earlier findings. We were interested in whether so-called three-way catalysts (TWC's) are equally unaffected. These catalysts, designed to remove NO, CO, and hydrocarbons simultaneously, are intrinsically much more prone to poisoning (1). In these laboratory experiments we were not concerned with catalyst deactivation by physical causes (plugging of catalyst pores and channels), which is an intrinsic problem associated with the deposits derived from MMT, even at lower concentrations (2, 8).

Apparatus and Materials

The pulse-flame apparatus has been described earlier in detail (9). However, some modifications were necessary to accommodate the testing of TWC's. The fuel mixture, consisting of isooctane vapor in heated nitrogen, and oxygen were preheated in a furnace kept at 500 °C. A second shorter furnace kept at 800 °C was used to ignite the fuel mixture as shown in Figure 1. With this arrangement, sufficiently high NO levels required for the testing of TWC's can be achieved. The temperature of the catalyst was adjusted by a third furnace. Catalyst activity was defined by the conversions of NO, CO, and hydrocarbons at 500 °C and an air/fuel ratio characteristic for the operation of TWC's.

Two basic fuels were used, isooctane and isooctane containing contaminants at levels typical for those gasolines required for the certification of engine systems by the Environmental Protection Agency. These contaminants were Pb [0.006 g/gal from tetraethyl lead (TEL) with lead scavengers], P [0.0008 g/gal from cresyl diphenyl phosphate (CDP)], and S (0.02 wt % from di-tertiary-butyl disulfide). We shall use the abbreviation "cert. fuel" for this contaminated isooctane. Manganese was added at a concentration of 0.125 g Mn/gal from MMT. However, some losses occurred in the liquid phase because of light-promoted oxidation (10), resulting in the formation of a precipitate. Thus, the actual concentration during this study was only 0.11 g Mn/gal.

Two monolithic catalyst formulations, TWC A and TWC B, were prepared by Engelhard Industries as prototypes for eventual use in exhaust systems operating under three-way conditions. These catalysts contain Pt and Rh.

Experimental Results and Discussion

Catalyst Deactivation Study. These tests were performed at an average space velocity of 40 000 h⁻¹, corresponding to a driving mode of 50 km/h (30 miles/h). The catalyst was subjected to temperature cycling between 370 and 760 °C to simulate thermal changes normally experienced by an auto-

otive catalyst. A CO concentration of 1.5% was adjusted by the flow of oxygen into the burner. The exhaust was adjusted further by the introduction of secondary oxygen upstream of the catalyst (cf. Figure 1) to simulate a suitable air/fuel ratio. The oxidation or reduction power of the exhaust gas here is defined by $R = (\text{CO} + \text{H}_2 + 19.2\text{HC})/(\text{CO}_2 + \text{NO})$, the ratio of the concentrations of the reducing and oxidizing gas molecules. The hydrogen concentration was not measured directly. Rather, it was approximated by one-third of the CO concentration, in accordance with the water gas shift equilibrium. A value of $R = 1.3 - 1.6$, which corresponds to an air/fuel ratio of 14.5 - 14.3 for a typical certification gasoline, was chosen in most cases. These conditions produced typically 550 ppm NO and 600 ppm HC (measured as hexane).

The activity of catalyst TWC A in the case of isooctane, without and with MMT, is shown as a function of time in Figure 2. Because the numerical values of CO and hydrocarbon conversions are similar, they are represented by one common line to simplify the graphs. At the end of the test, which corresponds to a simulation of about 40 000 km (25 000 miles), the catalyst samples show the same activity for both fuels.

Fresh samples of the same catalyst were then exposed to the combustion products of "cert. fuel" without and with MMT. The results are shown in Figure 3. Compared to isooctane, a pronounced deactivation is found with the addition of Pb, P, and S; however, the additional effects associated with the presence of MMT are quite insignificant. The corresponding curves measured on a catalyst of somewhat different composition (TWC B), shown in Figure 4, display a somewhat higher degree of divergence between the conversion percentages of the three pollutants. Moreover, it appears that the addition of MMT to "cert. fuel" favors NO conversion at the end of the test, while it affects hydrocarbon conversion adversely. The

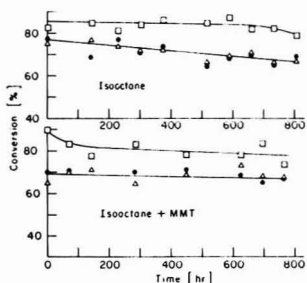


Figure 2. Deactivation of catalyst TWC A
Conversion of NO: \square , HC: Δ , and CO: \bullet in exhaust of isooctane and isooctane + MMT

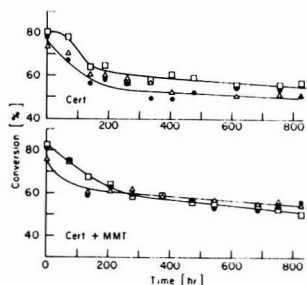


Figure 3. Deactivation of catalyst TWC A
Conversion of NO: \square , HC: Δ , and CO: \bullet in exhaust of isooctane containing certification additives without and with MMT

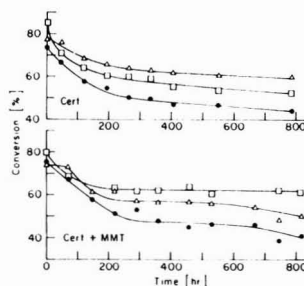


Figure 4. Deactivation of catalyst TWC B
Conversion of NO: \square , HC: Δ , and CO: \bullet in exhaust of isooctane containing certification additives without and with MMT

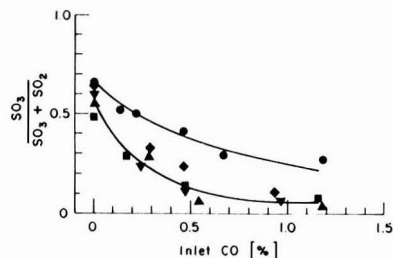


Figure 5. Production of sulfuric acid
Over TWC A, aging modes: fresh: \bullet ; isooctane + MMT: \blacklozenge ; certification additives: \blacktriangle ; certification additives + MMT: \blacksquare . Over TWC B: certification additives + MMT: \blacktriangledown

conversion differences are a decrease of about 10% in hydrocarbon conversion and a 10% increase in NO conversion. These changes are not very large and are probably partially caused by Mn deposits upstream of the catalyst.

The activity of catalysts containing metals of the Pt-group toward the formation of sulfuric acid was very sensitive to aging and poisoning, when measured as a function of CO concentration in previous pulse-flame tests (11). For this reason, we compared the catalyst buttons, aged in the MMT program, for their activity in the formation of SO_3 . This activity of a fresh sample of TWC A is represented by the top line in Figure 5. Activities measured on samples of TWC A and B aged with "cert. fuel" in the absence and presence of MMT are represented by the common lower line in Figure 5. Samples A and B aged with "cert. fuel" + MMT gave identical results, as shown in Figure 5.

Formation of sulfuric acid on a catalyst aged with isooctane containing MMT produced concentrations located between the two curves shown in Figure 5 as expected. Exactly as in the case of the three primary reactions (cf. Figures 2 and 3), catalysts aged by the combustion products of isooctane (with or without MMT) showed some deterioration (compared to a fresh catalyst) due to thermal aging, but less deterioration than that caused by certification additives. The results show that this secondary catalytic reaction is unaffected by Mn deposits.

Analyses of the catalyst buttons aged with MMT by x-ray fluorescence showed 0.5 wt % Mn. After exposure to Mn-free fuel for various times in the sulfate tests, the Mn deposits decreased to 0.16 - 0.45 wt %. A dislodgment of the rust-colored Mn deposit by exhaust from pure isooctane was also evident from visual inspection.

Catalytic Effects of Mn Deposits. During the aging experiments with MMT, deposits in the pulsator tube caused pronounced changes of the exhaust composition. These changes occurred *upstream* of the monolithic catalyst. If an automotive catalyst was present at all further downstream in the following experiments, its temperature was kept below 100 °C to render it inactive.

Figure 6 illustrates typical changes of the exhaust composition derived from isooctane with MMT as a function of time. In this experiment the CO concentration was adjusted to about 1.5%, and the *R* value to 1.6. A continuous decrease of the NO level from 600 ppm at the beginning to 75 ppm after 800 h occurred. In contrast, there was an increase of the hydrocarbon level from 500 to 700 ppm over 250 h, showing no further increase within the experimental error from then on. Such a continuous NO decline was not observed, when "cert. fuel" with MMT was used, as shown by the upper data points in Figure 7. The lower curve again shows the effects of MMT added to isooctane for a run which replicates the NO decrease with time, shown in Figure 6. Isooctane containing TEL, including scavengers (0.006 g Pb/gal), used as fuel after 850 h did not cause a change. However, when isooctane with 0.02 wt % S was introduced after 1000 h, a marked recovery of the NO level took place. A similar recovery was found in a second experiment. After operation with isooctane containing MMT, the fuel was switched to isooctane containing 0.008 g P/gal (tenfold the level used in "cert. fuel"). The recovery was even stronger than in the case of S, as shown in Figure 7. Practically complete recovery of the NO level also took place, within less than 200 h, when "cert. fuel" was used.

The cumulative nature of the Mn effect on the exhaust composition immediately suggests a catalytic action of the heavy wall deposits of the pulsator tube. Analysis by x-ray diffraction identified the fluffy deposits as Mn_2O_4 . Scrapings from the colder parts of the pulsator tube showed smaller particles, as indicated by rather diffuse lines. In addition,

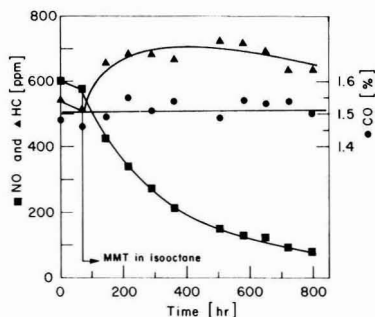


Figure 6. Changes of exhaust composition caused by deposits from MMT

NO: ■, HC: ▲, and CO: ●

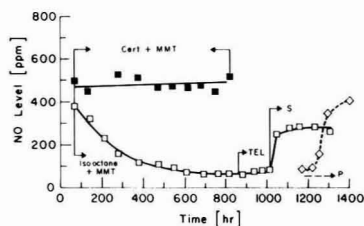


Figure 7. Effect of fuel contaminants on NO level in presence of Mn deposits

Table I. Comparison of Pollutant Levels for Isooctane and "Cert. Fuel" with MMT

Fuel	NO (ppm)	CO (%)	HC (ppm)
Isooctane	700	1.31	582
Cert. + MMT	718	1.30	585
Isooctane	690	1.28	580

Table II. Effects of Different Wall Deposits on Pollutant Levels

Pulsator tube after use with	NO (ppm)	CO (%)	HC (ppm)	R
Isooctane	575	1.41	580	1.27
Cert. + MMT	490	1.25	650	1.24
Isooctane + MMT	358	1.27	700	1.27
Isooctane	577	1.50	590	1.29
Cert. + MMT	520	1.35	690	1.21
Isooctane + MMT	402	1.33	717	1.26

$PbSO_4$ was found after the use of "cert. fuel" with and without MMT.

Oxides of Mn are effective oxidation catalysts. However, to interpret our results, additional experiments were necessary to answer several obvious questions. For example, it is of interest to know whether the NO is depressed by a catalytic reduction with hydrocarbons and CO after its formation, or whether it is not formed to begin with. Other questions concern the influence of Mn in the gas phase on the combustion products, and the degree of hydrocarbon and CO oxidation on the walls. For practical purposes, the influence of other fuel contaminants present in "cert. fuel" on the peculiarities associated with MMT is of interest.

The effect of Mn in the gas phase is treated first. Table I shows the pollutant levels in a clean pulsator tube produced by clean isooctane followed by combustion of "cert. fuel" with MMT at otherwise fixed conditions, especially at constant levels of primary and secondary oxygen. The pollutant levels in the two cases are identical within the experimental error. Therefore, the presence of gaseous Mn species in the combustion has little effect on the levels of pollutants produced.

In another series of experiments, different wall deposits were tested, while pure isooctane was burnt. Table II shows, for duplicate runs, the changes that took place when a clean pulsator tube was substituted by one used for about 800 h with fuels containing MMT. A sizable decrease in the concentrations of NO and CO and a comparable increase in hydrocarbons are found in the exhaust gas generated in the tube contaminated by Mn deposits from isooctane containing MMT. The same effect was noticed, albeit to a much smaller degree, when in addition to MMT the other fuel contaminants were present.

The concentration changes of NO and hydrocarbons, shown in Figure 6, appear aggravated in comparison to those of Table II. The difference originates from the successive adjustment of CO concentration, along with *R*, to constant values in the catalyst-poisoning experiments. While the CO is adjusted to compensate for oxidation losses on Mn deposits, concentrations of hydrocarbons and NO change concomitantly. Such changes might be partially responsible for small apparent differences in catalyst deactivation, as those described in connection with Figure 4.

The concentration changes of the reducing species, CO and hydrocarbons, in opposite directions as shown in Table II,

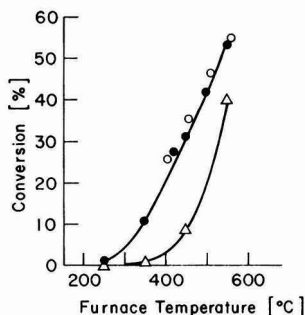


Figure 8. Catalytic effects of Mn deposits on oxidation of CO: ●, O; HC: △

Table III. Effect of External NO Addition to Exhaust

Addition of NO	NO (ppm)	CO (%)	HC (ppm)	R
None	122	1.61	680	1.39
Downstream	655	1.56	720	1.29
Into burner	635	1.39	1250	1.30
None	140	1.51	695	1.32

indicate a rather complex interaction. Indeed, when a synthetic mixture of 1.5% CO, 720 ppm propane, and 1.6% O₂ in heated nitrogen was passed through the pulsator tube coated with Mn₃O₄ from the operation of isooctane plus MMT, both CO and propane were catalytically oxidized, as shown in Figure 8. As the preheat furnace reaches the normal operating temperature of 500 °C, CO and propane conversions are 40 and 20%, respectively. In a clean tube, both conversions are insignificant.

The question concerning suppression of NO formation was evaluated by the addition of external NO. The results are given in Table III. The natural level of NO in a pulsator tube contaminated by the use of isooctane containing MMT was 122 ppm. When NO in nitrogen was added at the secondary inlet downstream of the combustion, while keeping the total nitrogen flow constant, the NO concentration increased to 655 ppm in agreement with the calculated amount. When the N₂-NO mixture was introduced through the nitrogen inlet of the burner at the same flow rate, no significant change in NO concentration was observed. However, the hydrocarbon concentration increased by the amount of NO added. These results demonstrate that the reduction of NO over the Mn deposits is not important.

The second effect, the increase of hydrocarbons, caused by the addition of NO was confirmed in several experiments. The nature of this phenomenon needs to be investigated further; it seems to be an intrinsic part of the combustion process and can be observed in the absence of Mn as well. Thus, when in a clean pulsator tube, 550 ppm of NO was added through the burner inlet, the exhaust showed an increase of NO by 75 ppm, and of hydrocarbons by 265 ppm. The relatively small increase of NO compared to the added NO is probably due to a depression of NO formation or decomposition of excess NO in the flame, in accordance with the value of the thermodynamic equilibrium.

The results lead to the tentative conclusion that the combustion temperature is artificially lowered by a partial oxidation of the fuel on the Mn deposits. In one extreme case, the

low-temperature oxidation predominated completely, and a flame pulse was no longer formed. Fuel oxidation was still complete, as shown by the remaining hydrocarbon level of a few hundred ppm. Less than 20 ppm of NO was formed in this case.

Conclusions

It appears that under our experimental conditions, Mn derived from MMT is converted in the combustion exclusively to Mn₃O₄. Recent analyses of deposits from engine systems also showed that this oxide was the end product in the oxidation of MMT. Although Mn₂O₃ is stable up to 940 °C, it loses oxygen above that temperature and the Mn₃O₄ produced does not revert to a higher oxide on cooling in air (12).

Since Mn₃O₄ is very stable, it is, in retrospect, not surprising that this compound does not react with the components of the catalyst. Deactivation, if any, would then appear to be limited to physical blockage of catalyst pores and channels. However, some interaction may be possible if the catalyst contains silica. It has been claimed in unpublished reports that silicates containing Mn can be formed on automotive catalysts under severe thermal stress. According to existing phase diagrams (13), such an event is unlikely under normal exhaust conditions.

With the development of emission control equipment of higher efficiency and sophistication, even subtle changes of the exhaust have to be viewed critically. Consideration must be given to the presence of catalytically active Mn deposits in the combustion chamber and exhaust system. Although the catalytic activity is largely, but not completely, poisoned by the small amounts of S and P that still remain in present gasolines, a careful evaluation of Mn deposits in engine systems seems to be in order. Engine studies would be required to determine to what extent the results observed in the laboratory can be expected during vehicle operation.

Acknowledgment

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New Oxide Catalysts with Perovskite-Related Structure for Reduction of Nitric Oxide with Ammonia

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■ Perovskite and its related K_2MgF_4 -type mixed oxides, $LnMO_3$ and Ln_2MO_4 (Ln : lanthanoid, M : 3d-transition element), are examined as potential catalysts for reduction of nitric oxide (NO) with NH_3 . Some cuprates such as Gd_2CuO_4 and Zr-doped La_2CuO_4 exhibit promising characteristics. When a gas system consists simply of NO and NH_3 (diluted with N_2), reduction of NO takes place according to $6NO + 4NH_3 = 5N_2 + 6H_2O$, and conversion of NO increases with an increase in temperature up to 400 °C. Under conditions where O_2 exists in the system, conversion of NO has a sharp maximum at a temperature near 250 °C. When SO_2 is added or catalysts have adsorbed it, reduction of NO takes place according to $4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$, and conversion of NO does not decrease although O_2 is present. Life expectancy tests of a supported Zr-doped La_2CuO_4 catalyst, conducted at 350 °C with a synthetic gas whose composition is similar to that of a boiler flue gas, show that a conversion efficiency of 90% (at the gas flow rate per unit catalyst volume of 6000 cm^3 (STP)/ cm^3 /h) is maintained for more than 2000 h.

Compounds such as (La, Sr) CoO_3 with the perovskite structure attracted attention as oxygen electrode catalysts for alkaline solution in the early 1970's (1, 2). We have studied similar compounds to develop a new type of air electrode for air/zinc batteries (3). These compounds facilitate not only the electrochemical reduction of oxygen but also many other redox reactions in a wide range of temperatures. This finding prompted us to investigate them as possible reduction catalysts for nitrogen oxides. The work conducted by Libby (4) and Voorhoeve et al. (5) who applied similar compounds to CO reduction catalysts for automobile emission control was undertaken after Meadowcroft's enlightening work on $LaCoO_3$ oxygen electrode catalysts (1).

As we previously reported, these perovskite-type mixed oxides have high electronic conductivity (i.e., 10^0 – 10^4 $\Omega^{-1} cm^{-1}$) as well as an extraordinarily large oxygen diffusivity (i.e., 10^{-11} cm^2/s at 25 °C for $Nd_{0.8}Sr_{0.2}CoO_3$) (6, 8). These oxides take oxygen-deficient nonstoichiometric compositions in reducing atmospheres, and the reoxidation takes place reversibly. Catalytic activity for the electrochemical reduction of oxygen is interpreted in connection with these properties.

We have examined these perovskite-type compounds as well as those like La_2NiO_4 , having a closely related structure, as a catalyst for reduction of NO with NH_3 . The latter, whose structure is considered a kind of two-dimensional analogue of perovskite, exhibits almost the same properties as those with the perovskite structure. Of the numerous candidates for reducing agents, NH_3 has been chosen because it is considered to be most suitable for stationary plant uses for economic and safety reasons. In this paper, we report the results of the examination and some detailed properties of a supported $La_2(Cu,Zr)O_4$ catalyst, selected by screening, with emphasis on the influence of SO_2 .

Experimental

Sample Preparation. Pellet-Type Catalyst. As starting materials, acetates of the component elements were used, with

the exception of zirconyl nitrate and ferric ammonium citrate which were used for sources of Zr and Fe, respectively. The desired amount of reagents was weighed and dissolved in pure water to give a solution of the component metal salts. This solution was then evaporated at temperatures between 80 and 90 °C under an aspirator vacuum using a rotary evaporator. The residue, a homogeneous mixture of the component salts, was placed in a quartz boat and calcined at 900 °C for 4 h in air. Thus, the obtained powder was checked by x-ray diffraction to see if the attempted compound had been formed.

An aqueous solution of polyvinyl alcohol (10 wt %) was added to this powder to form a paste, and it was molded into a pellet 3 mm diameter and 2 mm height. The pellets were then sintered at 750 °C for an hour in air and used as a specimen catalyst. The BET surface area of these catalysts lay between 7 and 9 m^2/g , and their porosity was about 50% in each case.

Supported Catalyst. As a catalyst carrier, spheric (3 mm ϕ) and ring-shaped (7 mm ϕ \times 2 mm ϕ \times 6 mm) γ - Al_2O_3 were used. Their BET surface area and pore volume before impregnation were about 200 m^2/g and 0.3 mL/g, respectively. These carriers were impregnated with a similar solution as above, and then calcined at 900 °C for an hour in air. Amounts of the impregnated oxide catalyst were controlled by both concentration of solution and impregnation conditions. Catalysis used in the present study contained about 7 weight % of mixed oxide ($La_2Cu_{0.9}Zr_{0.1}O_4$). Their BET surface area and pore volume after sintering were 80–120 m^2/g and about 0.4 cc/g, respectively.

Experimental Apparatus. Experiments were carried out using an ordinary gas flow system at atmospheric pressures. The pellet-type and the spheric 3-mm catalysts were tested using horizontally upheld Pyrex glass tubes with diameters of 10 and 15 mm ϕ , respectively. The ring-shaped catalysts were tested in a vertically upheld tube with a diameter of 36 mm ϕ . Ammonia was added immediately before the catalyst bed to protect it from reacting with other species at lower temperatures. Special attention was paid to a structure of the nozzles so that NH_3 could be mixed well because the distance between the catalyst bed and the NH_3 nozzle was so close.

Although linear velocities of gases underwent a wide range of change as gas flow rates per unit volume of catalyst and diameter of the reaction tubes were changed, no influence on the conversion of nitrogen oxides was observed, suggesting that the reaction rate is determined only by the space velocity within the range of linear velocities employed in this study as long as other parameters are kept constant.

Analyses. Concentrations of NO at the inlet and the outlet of a reaction tube were continuously monitored with a chemiluminescence NO analyzer (CLA-21, Horiba Co., Japan). Calibration of the NO meter was carried out using standard gases whose NO concentration had been checked both by the nitric acid titration method and the Saltzman method.

Detection of N_2O in the outlet gas was conducted with an infrared gas analyzer with a gas cell having a 100-cm optical path, which was estimated to have sensitivity of 8 ppm when an adsorption band at 4.5 μm was used.

The concentration of NH_3 was measured by the Indophenol

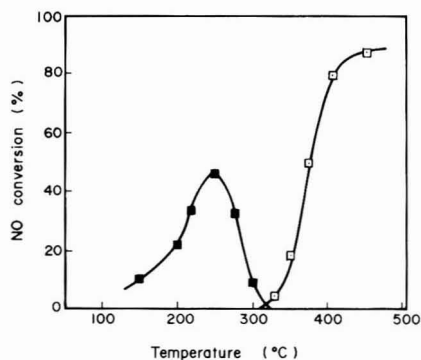


Figure 1. Temperature dependences of NO conversion for LaCoO_3 at gas flow rate per unit volume of catalyst of 3000 cm^3 (25°C , 1 atm)/ cm^3/h
 ■ NO, 460 ppm; NH_3 , 830 ppm; O_2 , 7700 ppm. □ NO, 460 ppm; NH_3 , 830 ppm; O_2 , free

method according to JIS (Japan Industrial Standard) K 0099 (9).

Continuous monitoring of SO_2 was conducted using a nondispersion-type infrared gas analyzer (ESDA-200, Horiba Co., Japan), which had the accuracy of 20 ppm at the measuring range of 2000 ppm.

Results and Discussion

Search for Catalysts. As a typical example for a series of compounds, $\text{Ln}_{1-x}\text{M}_x\text{CoO}_3$ (Ln = lanthanoid, M = Ca, Sr, and Ba), temperature dependences of NO conversion for the pellet type LaCoO_3 catalyst are shown in Figure 1. When the inlet gas consists merely of NO and NH_3 (and N_2 as a balancing gas), conversion of NO becomes prominent at temperatures around 320°C and thereafter increases simultaneously with an increase of temperature.

On the other hand, when O_2 coexists with NO and NH_3 , the shape of NO conversion takes a sharp maximum at tempera-

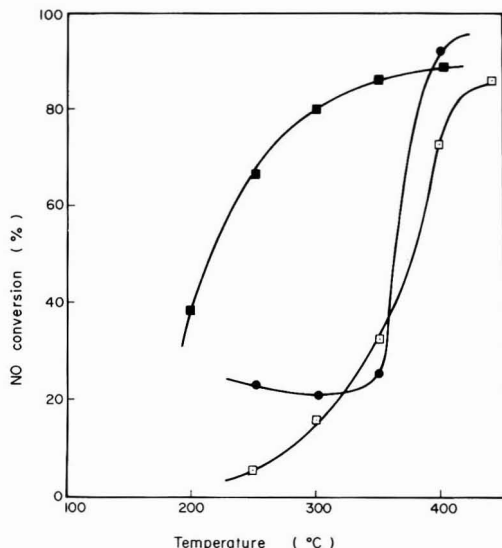


Figure 2. Temperature dependences of NO conversion for compounds with K_2MgF_4 structure
 Inlet gas composition: NO, 460 ppm; NH_3 , 830 ppm; O_2 , free. Gas flow rate per unit volume of catalyst: 3000 cm^3 (25°C , 1 atm)/ cm^3/h . □ La_2NiO_4 , ● $\text{La}_{1.5}\text{Sr}_{0.5}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_4$, ■ La_2CuO_4

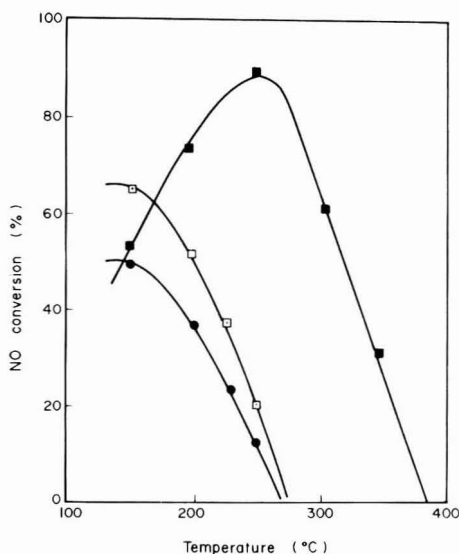


Figure 3. Temperature dependences of NO conversion for compounds with K_2MgF_4 structure

Inlet gas composition: NO, 460 ppm; NH_3 , 830 ppm; O_2 , 7700 ppm. Gas flow rate per unit volume of catalyst: 3000 cm^3 (25°C , 1 atm)/ cm^3/h . Symbols same as in Figure 2

tures near 250°C , indicating that O_2 plays a role as a promoter on reduction of NO with NH_3 in the temperature region under 250°C . At higher temperatures, however, conversion of NO decreases rapidly with an increase of temperature, presumably due to a side reaction, i.e., oxidation of NH_3 with O_2 . Such an effect of O_2 as shown here has been also reported by Markvart and Pour (10) for the case of reduction of NO with NH_3 on a CuO catalyst, suggesting that there are no fundamental differences in the reaction mechanism between CuO and the present catalysts.

Either for oxides in which La had been partly substituted by Sr ($\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$; x 0.5) or for those in which La had been totally substituted by other rare earths (i.e., Pr, Nd, Sm, and Gd), the results were almost the same as shown in Figure 1. In addition, LaNiO_3 , synthesized using a flux method according to Wold et al. (11), has been also tested as a typical example of a series of the perovskite compounds other than cobaltites. This compound exhibited a little higher activity on NO reduction, but its dependence on temperature and behavior with regard to coexisting O_2 is essentially the same that was observed for cobaltites.

Figures 2 and 3 show typical results for compounds having a K_2MgF_4 structure, a kind of two-dimensional analog of the perovskite. Compound La_2NiO_4 and its modification show characteristics similar to those of LaCoO_3 , except that the curves in the figures, regardless of whether O_2 exists or not, shift to the lower temperature side at approximately 50°C .

Contrary to these, La_2CuO_4 exhibits much higher activities; i.e., it facilitates NO reduction at temperatures as low as 200°C even in the absence of O_2 , and the O_2 depression of La_2CuO_4 is shifted to higher temperatures as compared with La_2NiO_4 or LaCoO_3 (Figure 3).

This result prompted us to investigate the lanthanoid-copper oxide series as potential catalysts. Figure 4 shows NO conversion under the presence of O_2 for various Ln_2CuO_4 (Ln : lanthanoid) as a function of ionic radii of Ln^{3+} . Lanthanoid heavier than Gd and tetravalent Ce do not form a compound with K_2MgF_4 structure. Catalytic activities decrease with an

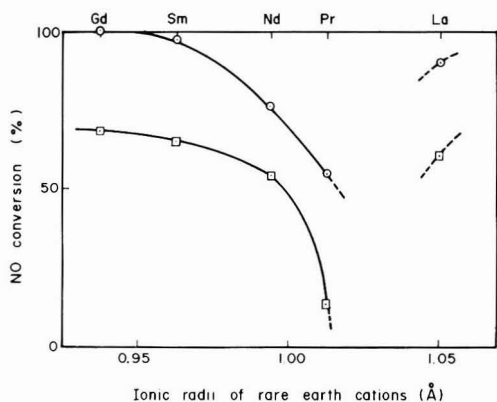


Figure 4. Relation between catalytic activity and ionic radii of Ln^{3+} in Ln_2CuO_4 at 250 °C (O) and 300 °C (□)

Inlet gas composition: NO, 460 ppm; NH_3 , 830 ppm; O_2 , 7700 ppm. Gas flow rate per unit volume of catalyst: 3000 cm^3 (25 °C, 1 atm)/ cm^3/h

increase in ionic radius from Gd to Pr, but La_2CuO_4 takes anomalously high values of NO conversion.

It is difficult to give a detailed explanation for the variation of catalytic activities with Ln^{3+} radii, but it may be reasonable to consider since this is caused by a change in the electron configuration of Cu^{2+} , which is surrounded by six oxygen ions in the crystal lattice. Note that the trend of catalytic activities shown in Figure 4 correlates very well with those of electrical conductivities and the Seebeck coefficients reported by Kenjo and Yajima (12) for the same series of compounds; a slope for the plots of the Seebeck coefficient vs. $1/T$ increases as the size of rare earth cations decreases from Pr to Gd. These experimental results have been interpreted as an effect of energy level changes in the 3d electrons in Cu^{2+} (or Cu^+) caused by a change of ligand fields.

Irregularity of catalytic activities observed between Pr and La may likewise be accounted for as a large change in the ligand fields accompanied by a discontinuity of lattice parameters seen in the relevant interval. X-ray diffraction shows that La_2CuO_4 has a monoclinic unit cell ($Z = 4$), which is a distorted structure of the tetragonal one observed in other Ln_2CuO_4 . The angle between the a and c axis is 89.58°, and the lattice constant of a (= b) axis is 3.82 Å, which is smaller than 3.96 Å for Pr_2CuO_4 in spite of the fact that the radius of

La^{3+} is larger than Pr^{3+} . To compensate for this, the c axis (13.20 Å) expands more than expected by an increase in ionic radii. This structural anomaly, which brings about a new electronic interaction between Cu^{2+} and O^{2-} in the x-y direction, gives a metallic conduction to it, which is not seen for other compounds in the same series, and irregular catalytic activities as well.

The above discussion suggests that catalytic activities could be controlled by substituting metal ions in La_2CuO_4 by others that would cause a desirable electronic state around Cu^{2+} . We have therefore synthesized a series of compounds, $\text{La}_2\text{Cu}_{1-x}\text{M}_x\text{O}_4$, and tested their catalytic activities in the reduction of NO with NH_3 . Results are tabulated in Table I, where activities are demonstrated in terms of NO conversions at 300 °C (NO + NH_3) and 250 °C (NO + NH_3 + O_2). A significant improvement in catalytic activities can be seen for samples doped with Al or Zr, although a detailed mechanism is not evident at this time.

Supported $\text{La}_2\text{Cu}_{0.9}\text{Zr}_{0.1}\text{O}_4$ (LCZ) Catalyst. Since screening of catalysts suggested the use of LCZ, we prepared a support-type LCZ, a more practical form of catalyst, and examined its fundamental characteristics. Behaviors of supported LCZ shown in Figure 6 (two curves marked by "SO₂ free") are not greatly different from those of pellet-type LCZ, except that the rate of NO reduction for the former is much larger than that for the latter. The gas flow rate per unit volume or catalyst employed in Figure 1 was 3000 h^{-1} , and 6000 h^{-1} in this figure. This improvement in activity is due to the larger surface area of supported catalysts. The specific surface area of supported LCZ is approximately 100 m^2/g compared with 8 m^2/g for pellet-type catalysts, although it is not clear how many open pores are covered by LCZ.

To evaluate the possibility of applying LCZ to the boiler flue gas treatment, the influence of SO₂, usually contained in it, has been checked. These experiments revealed a distinctive feature of this catalyst.

Figure 5 depicts the changes associated with the introduction of SO₂ to the catalyst bed at 350 °C. In the first hour, SO₂ was not added, so that a variation of outlet NO concentration for NO + NH_3 + O_2 system could be seen. The change was rather slight, and the NO concentration reached a constant value of 495 ppm against its inlet concentration of 1000 ppm. At this time, SO₂ was introduced to the system with the other conditions remaining unchanged. This caused a remarkable decrease in outlet NO concentration, indicating SO₂ played a role as a promoter in the reduction of NO. The concentration

Table I. Catalytic Activities of $\text{La}_2\text{Cu}_{1-x}\text{M}_x\text{O}_4$

$\text{La}_2\text{Cu}_{1-x}\text{M}_x\text{O}_4$	Conversion of NO (%) ^a	Conversion of NO (%) ^a	
		NO + NH_3 , 300 °C	NO + NH_3 + O_2 , 250 °C
Li 0.1	10	32	
Al 0.1	100	98	
Ti 0.05	21	60	
Cr 0.1	67	67	
Mn 0.1	73	46	
Fe 0.1	75	94	
Co 0.1	59	46	
Ni 0.1	77	89	
Ni 0.5	10	38	
Zn 0.1	48	37	
Zr 0.05	91	99	
Zr 0.1	89	100	

^a Inlet gas composition: NO, 460 ppm; NH_3 , 830 ppm; O_2 , 7700 ppm or none. Gas flow rate per unit volume of catalyst: 3000 cm^3 (STP)/ cm^3/h .

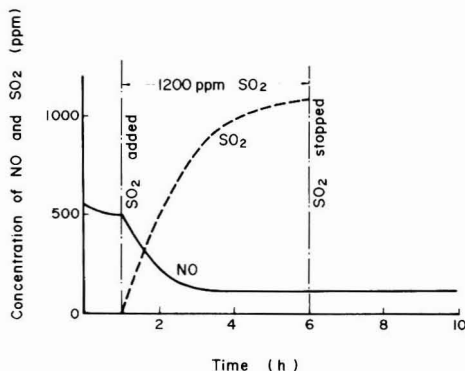


Figure 5. Effect of SO₂ on reduction of NO for supported $\text{La}_2\text{Cu}_{1-x}\text{Zr}_x\text{O}_4$ ($x = 0.1$) catalyst

Inlet gas composition: NO, 0.1%; NH_3 , 0.1%; O_2 , 1.0%; SO₂, 0.12% or none. Gas flow rate per unit volume of catalyst: 6000 cm^3 (25 °C, 1 atm)/ cm^3/h . Temp, 350 °C

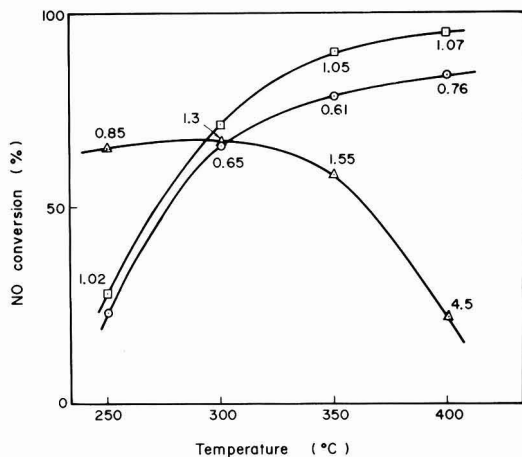


Figure 6. Temperature dependences of NO conversion and ratios of NH_3 : NO consumed in reaction process for supported $\text{La}_2\text{Cu}_{1-x}\text{Zr}_x\text{O}_4$ ($x = 0.1$) catalysts

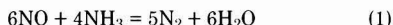
○ SO_2 free catalyst, (NO 0.1% + NH_3 0.1%). Δ SO_2 free catalyst, (NO 0.1% + NH_3 0.1% + O_2 1.0%). \square Catalyst adsorbing SO_2 , (NO 0.1% + NH_3 0.1% + O_2 1.0%). Numerical values represent NH_3 : NO (consumed). Gas flow rate per unit volume of catalyst: $6000 \text{ cm}^3 (25^\circ\text{C}, 1 \text{ atm})/\text{cm}^3/\text{h}$

of SO_2 in the outlet gas was simultaneously measured, which is shown in the figure as a dotted line. Immediately after introduction, the concentration of SO_2 was very low, indicating that almost all SO_2 added was consumed in the catalyst bed. Then, it gradually increased as time elapsed and NO concentration began to decrease.

It is therefore reasonable to believe that SO_2 adsorbed on the catalysts facilitates the reaction between NO and NH_3 . Note that very little SO_3 was detected in the outlet gas. The supply of SO_2 was cut off after 6 h when the outlet SO_2 concentration reached almost the same value as the inlet concentration (1200 ppm). With the supply cut off, no change in outlet NO concentration was observed for more than 4 h afterward. Another experiment conducted under similar conditions proved that once the catalyst adsorbs SO_2 , its effect lasts for more than 100 h so long as O_2 is present.

There would be several alternative reasons to suspect that SO_2 has a role in the reduction of NO with NH_3 . Of these, however, it seems most likely that SO_2 facilitates the reaction as a result of its suppressive effect upon the side reactions between NH_3 and O_2 . To prove this, ratios of NH_3 to NO consumed in the catalyst bed, defined by ξ , were measured under three typical conditions as shown in Figure 6. In these experiments, effects of SO_2 were examined using catalysts pretreated in an atmosphere containing 1200 ppm of SO_2 and 1% of O_2 , for 5 h at 350°C , instead of passing SO_2 to prevent it from reacting with NH_3 during measurements.

The parameter ξ for the catalyst free from SO_2 shows values near 0.67 throughout the temperature range between 250 and 400°C so long as O_2 does not exist in the reaction system, indicating that NO reacts with NH_3 according to



When O_2 exists, however, ξ for the same SO_2 free catalyst shows values much larger than those for the above case. Conversion of NO rapidly decreases as ξ increases at a higher temperature, indicating that side reactions between NH_3 and O_2 , i.e., oxidation of NH_3 with O_2 , prevail over the reduction of NO with NH_3 .

On the other hand, the temperature dependence for the catalyst-adsorbed SO_2 resembles that for the O_2 -free case

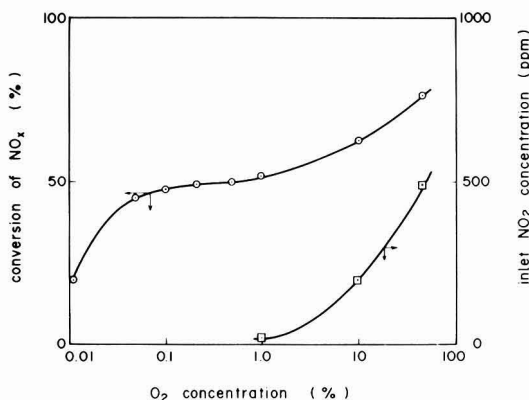
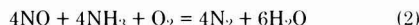


Figure 7. Relation between NO_x conversion and O_2 concentration for supported catalyst adsorbing SO_2

Inlet gas composition: NO + NO_2 , 950 ppm; NH_3 , 920 ppm. Gas flow rate per unit volume of catalyst: $20000 \text{ cm}^3 (25^\circ\text{C}, 1 \text{ atm})/\text{cm}^3/\text{h}$. Temp, 340°C

above although O_2 is present in this case. Nevertheless, ξ 's observed here do not show 0.67, but values near 1.0 in the same temperature range. Assuming ξ to be unity, i.e., NO reacts with NH_3 in the ratio 1:1, the reaction in this case would be



since it has been confirmed by IR analysis that no nitrogen oxides other than NO were present in the outlet gas. This equation implies that O_2 is indispensable in the advancement of reduction of NO with NH_3 on the surface of the catalyst-adsorbed SO_2 .

In fact, NO reduction decreases with a decrease in O_2 concentration as shown in Figure 7, where one of the ordinates is the conversion of total nitrogen oxides because NO_2 is inevitably formed in the inlet gas at higher O_2 concentrations. Further details on the role of SO_2 in the reduction of NO are under study and will be published elsewhere.

We have conducted bench scale tests under conditions that resemble those for the boiler flue gas treatment, using 7-mm ϕ ring-shaped catalysts packed in a larger reaction tube having a diameter of 36 mm ϕ . Figure 8 shows the relations between

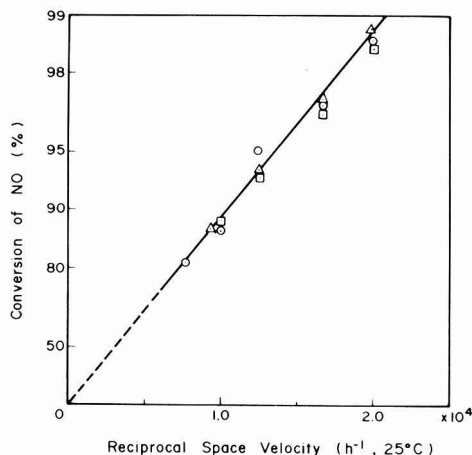


Figure 8. Relation between gas flow rate (25°C , 1 atm) per unit volume of catalyst and NO conversion at 350°C

Inlet gas composition: Δ NO, 200 ppm; \circ 400 ppm, \square 700 ppm. NH_3 1:1 with respect to NO, SO_2 0.1%, O_2 3.0%, CO_2 12%, H_2O 12%, N_2 balance

gas flow rates per unit volume of catalyst and NO conversion at 350 °C for three cases of inlet NO concentrations ranging from 200 to 700 ppm. Ammonia was added so that its concentration at the inlet of catalyst bed became equal to that of NO.

Plots of logarithmic NO conversion vs. reciprocal gas flow rate show a linear relation, and NO conversions do not depend on initial NO concentration, indicating that the kinetics of the relevant reaction is first order with respect to NO concentration. In these experiments, which differed from previous ones, 12% of the H₂O and CO₂ was contained in the reaction gases. The NO conversion was not affected by the presence of CO₂ but decreased a little (about a 10% decrease in the rate constant) in the presence of 10% H₂O. This seems reasonable since diffusion of H₂O, resulting from the reaction, from the surface of the catalyst to the bulk gas phase may be suppressed by the presence of H₂O in the bulk gas phase.

A continuous life expectancy test, conducted using a synthetic gas with the same composition as Figure 8, revealed that catalytic activities showed no change for at least 2000 h. However, life expectancy tests in the presence of SO₃ showed that the life of the catalyst is considerably affected. Degradation may arise mainly from a decrease in surface area accompanied by formation of Al₂(SO₄)₃ as a result of the reaction between alumina carriers and SO₃. The influence of SO₃ became more serious at lower temperatures. At 300 °C the ratio of an apparent rate constant for NO reduction to its initial value became 50% after a period of 200 h in the case of the presence of 50 ppm SO₃, whereas it was only a few percent at 350 °C for the same period. Note, however, that degradation

of SO₃ is not a fatal problem for application of this catalyst to flue gas treatment, supposing this catalyst is applied to flue gases containing SO₃ less than 10 ppm at temperatures more than 350 °C.

In a pilot plant test with a scale of 4000 nm³/h, the supported LCZ catalyst exhibited characteristics almost as good as those shown in Figure 8, and they were maintained for several thousand hours. An exhaust gas was used with temperatures of 350–400 °C drawn from the outlet of an economizer of an electric power plant boiler. The details of this pilot plant test will be reported at a later date.

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Electron-Beam Oxidation Treatment of a Commercial Dye by Use of a Dual-Tube Bubbling Column Reactor

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■ A flow method study on electron-beam oxidation treatment of a commercial azo dye (Acid Red 265) aqueous solution was carried out using a five-stage, dual-tube bubbling column reactor. Experiments were performed at ambient temperature over the ranges of the inlet dye concentrations from 50 to 400 ppm, and the solution feed rates from 1.5 to 10 L/min, the oxygen bubbling rates from 0.5 to 3.0 L/min for each column, and the mean dose rates from 0.4 to 1.6×10^5 rad/s in the penetration range of electron. The electron-beam decoloration of the dye aqueous solution was successfully attained in a flow system. The dissolved oxygen was maintained at a high concentration by using this type of reactor for the high dose rate irradiation in the range. The amounts of oxygen consumed in the initial stage were much larger than those of OH radicals formed by the radiolysis of water, and the rate of oxygen consumption decreased as the decoloration proceeded in later stages.

For radiation treatment of wastewater, an electron accelerator is a promising radiation source from the viewpoint of safety in handling and larger energy output compared with radioactive isotopes (1). In oxidation decomposition of phenol aqueous solution by electron beam in a thin-layer continuous flow-type reactor, the oxygen dissolving becomes a rate determinant factor with an extremely high dose rate (2).

To overcome this problem, we proposed a concentric dual-tube bubbling column as a reactor for the oxidation treatment of wastewater by electron beam. In the present paper, this type of reactor is demonstrated for electron-beam decoloration of azo dye (Acid Red 265) aqueous solution. Colored wastewater from dye or textile industries does not degrade easily by a conventional method such as activated sludge process. Suzuki et al. carried out basic studies on decoloration (3) and degradation (4) of various dye aqueous solutions by γ -rays from ⁶⁰Co. They reported that the decoloration of Acid Red proceeded by attack of the OH radical formed by the radiolysis of water, and that the dye molecules were degraded to lower molecular weight compounds, and finally to carbon dioxide. The degradation reaction was promoted by dissolved oxygen.

This study examines the performance of this type of reactor from the viewpoint of reaction engineering by using decoloration of a dye, and proves that this reactor can maintain the dissolved oxygen at a high concentration under high dose rate irradiation by an accelerator.

Experimental

Apparatus. A flow sheet of the experimental apparatus is presented in Figure 1. Shown are the reactor which is composed of five columns, the nonseal-type solution feed and

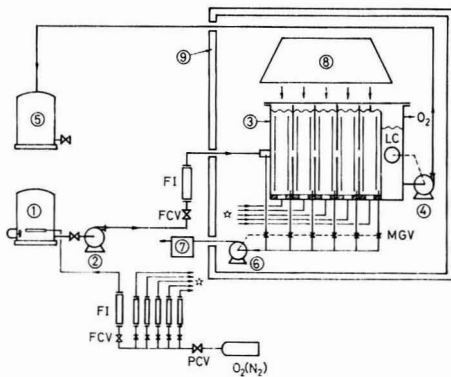


Figure 1. Flowsheet of experimental apparatus
 1. Solution tank, 2. solution feed pump, 3. reactor, 4. solution exhaust pump, 5. irradiated solution tank, 6. sampling pump, 7. analyzers, 8. accelerator, 9. hot cell

exhaust pumps (30 and 50 L/min in maximum capacity), the bellows-type sampling pump (300 mL/min), the solution tank (1.2 m³), the irradiated solution tank (3 m³), and analyzers. In this figure, FI, FCV, PCV, MGV, and LC designate rotameter, flow rate control valve, pressure control valve, magnetic valve for sampling, and liquid-level controller, respectively. The equipment that comes in contact with the solution is made of stainless steel (SUS-304).

The unit column, detailed in Figure 2, is a bubbling column equipped with a draft tube. Oxygen gas is bubbled into the inner tube from the bottom. The lift force of bubbles causes upward and downward streams in the inner and annular portions, respectively, and the solution circulates in the column. When the reactor is irradiated from the topside as shown in Figure 1, the surface portion in the penetration range of the electron is the reaction zone, and the portion under the range is the oxygen absorption zone. Since the solution flows out from the irradiation zone and reenters the oxygen absorption zone before the dissolved oxygen (DO) is consumed completely, the DO in the reaction zone can be maintained at a high concentration.

The reactor is a five-stage, dual-tube-type bubbling column, with a 50- μ -thick stainless steel entrance window of electron beams. Each column is 78.1 mm ϕ in inner diameter and 4.0 L in volume, and has a draft tube of 800^l \times 47.8^l \times 1.5^l mm, and a gas bubbler with a perforated plate at the bottom, which has 25 holes of 0.5 mm ϕ . Adjacent columns are connected

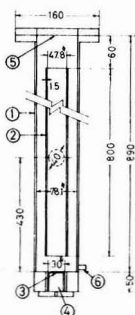


Figure 2. Column unit
 1. Outer tube, 2. draft tube, 3. perforated plate, 4. gas chamber, 5. beam entrance, 6. sample outlet

through a hole of 40 mm ϕ , and the solution level in the reactor is maintained constant by overflowing from the sluice of the fifth column.

The accelerator is an electron beam generator from the General Electric Co., Ltd. The energy of the electron beam is 2 MeV maximum, with the beam current being variable from zero to 6 mA.

Preparation of Solution and Analysis. The solution was prepared by dissolving Acid Red 265 (Kayaku Acid Brilliant Red BL from Nippon Kayaku Co., Ltd.) without further purification in ion-exchange water that did not contain organics by TOC measurements. The commercial dye contained sodium sulfate which does not affect decoloration, and its 100 ppm is equivalent to 60 ppm of purified Acid Red 265. In this report the concentration of dye pertains to that of the commercial dye.

The degree of decoloration was determined by measuring the optical density at 542 nm with a Shimadzu spectrophotometer UV-200. The concentration of DO was determined by using "Fieldlab" from Toshiba-Beckman Co., Ltd. The pH was determined by a TOA HM-18 B pH meter.

Irradiation Procedure. The dye aqueous solution was prepared in the solution tank and bubbled at about 10 L/min of oxygen under agitation for about 1 h. The oxygen-saturated solution was fed at the required flow rate by the solution feed pump to the reactor, in which oxygen was again bubbled in each column. When the solution flow reached steady state, the irradiation was started. The reaction reached steady state after about 20 min irradiation. The irradiated solution was sampled out from each column by the sampling pump, and the absorption spectra, DO concentration, and pH were measured. The main flow from the fifth column was led to the irradiated solution tank. The experiments were carried out at ambient temperature over the ranges of the inlet dye concentrations from 50 to 400 ppm, the solution feed rates from 1.5 to 10.0 L/min, the oxygen bubbling rates from 0.5 to 3.0 L/min for each column, and beam currents from 1.0 to 3.0 mA.

Some experiments were carried out in a nitrogen bubbling system. In these experiments nitrogen gas was bubbled in both the solution tank and reactor.

Dose Rate Measurements. The mean dose rate in the reaction zone was determined by Fricke dosimetry [$G(\text{Fe}^{3+}) = 8.2$ for nitrogen bubbling]. Glass vessels just fitted to the columns were placed in five columns, nitrogen-bubbled Fricke solution was poured into the vessels, and the liquid depth was adjusted to the penetration range of electron. The range for each column was determined by examining the depth dose curve which was measured by irradiation of piled CTA (cellulose triacetate) films 125 μ thick (5).

The Fricke solution was irradiated for 10 s at 1 mA, and the mean dose rate in the range for each column was determined as shown in Table I.

Measurements of Circulation Flow Rate in Column. Although estimation methods of the circulating flow rate in a dual-tube-type bubbling column were discussed by Itagaki et al. (6) and Takasaka et al. (7), an accurate method of cal-

Table I. Penetration Range of Electron and Mean Dose Rate in Range for Each Column

	Column				
	1st	2nd	3rd	4th	5th
Dose rate (Mrad/s/mA)	0.0400	0.053	0.0517	0.0517	0.0378
Range (g/cm ²)	0.650	0.705	0.705	0.690	0.675

Table II. Circulating Flow Rate and Capacity Coefficient in Column

	Feed rate (L/min)	Gas bubbling rate (L/min)			
		0.5	1.0	2.0	3.0
Circulating flow rate (L/min)	2.5	...	25.0
	5.0	18.2	25.5	31.6	32.0
Capacity coefficient (s ⁻¹)	1.5	...	0.024
	2.5	...	0.020
	5.0	0.013	0.019	0.056	0.087
	10.0	...	0.022

ulation has not been established. In this study the circulating flow rate was determined experimentally by examining the period of liquid circulation from responses of electric conductivity to a pulse input of electrolyte (sulfuric acid) into the column. A tungsten cell was placed in the annular portion at the measurement.

The period was determined from the time interval from peak to peak in the response curve. The mean circulating flow rate can be estimated from the period and the total volume of the solution in the column. The flow rates obtained are summarized in Table II. The circulating flow rates depend only on the gas bubbling rate and do not depend on the solution feed rate.

Measurements of Capacity Coefficients of Oxygen Absorption. The capacity coefficient was also determined experimentally. In these experiments the nitrogen-bubbled water was fed to the reactor where oxygen gas was bubbled without irradiation, and the DO concentrations of the inlet and outlet of the column were measured. Since the liquid film capacity coefficient can be regarded to be much smaller than that of the gas film in this bubbling column, the overall capacity coefficient is calculated by Equation 19 derived in the Appendix. The capacity coefficients obtained are listed in Table II. They also depend on only the gas bubbling rate, but do not depend on the water feed rate.

Results and Discussion

Change of Absorption Spectra of Irradiated Solutions. The absorption spectra of irradiated solutions under oxygen

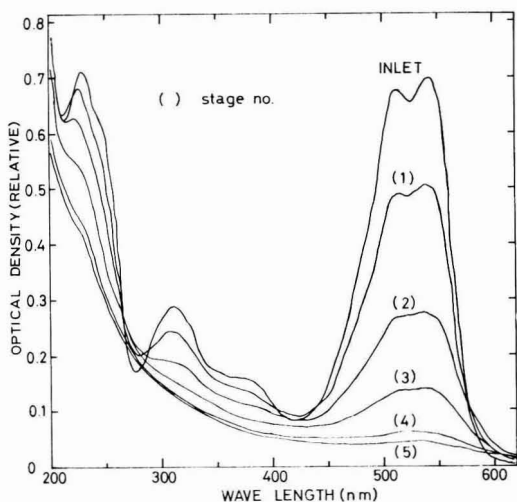


Figure 3. Absorption spectra of irradiated solutions in oxygen bubbling system
Solution feed rate, 5.0 L/min; inlet concentration of dye, 100 ppm; gas bubbling rate, 1.0 L/min; beam current, 2 mA

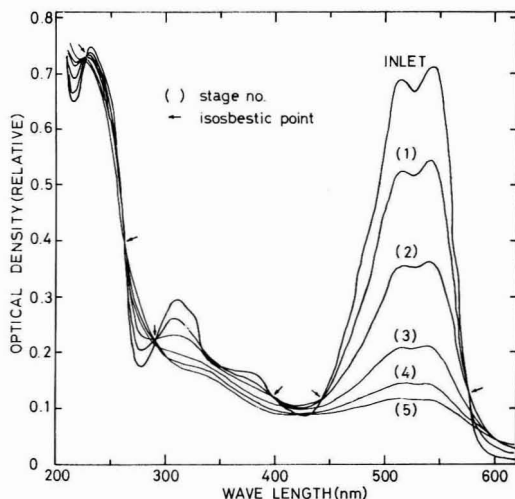


Figure 4. Absorption spectra of irradiated solutions in nitrogen bubbling system
Solution feed rate, 5.0 L/min; inlet concentration of dye, 100 ppm; gas bubbling rate, 1.0 L/min; beam current, 2 mA

and nitrogen bubbling are shown in Figures 3 and 4. The absorbances at 542 and 310 nm decreased with irradiation under both oxygen and nitrogen bubbling, but absorbance at 230 nm is influenced markedly by oxygen and does not decrease easily under nitrogen bubbling. Since the absorption at 230 nm is due to the substituted aromatic rings, the decrease may mean that the aromatic rings are decomposed by irradiation under oxygen bubbling. For low conversion the isosbestic points are observed at six different wavelengths as seen in Figure 4. These isosbestic points were also observed in batch experiments by γ -ray (3).

Decoloration and pH Change with Irradiation. The degree of decoloration in a column, η , is defined as

$$\eta = \frac{A_0 - A}{A_0} \quad (1)$$

where A_0 and A are the optical densities at 542 nm for the reactor inlet and sampled solutions from the column. Typical results of the degree of decoloration and pH for each column are plotted in Figure 5. The electron-beam decoloration of the dye aqueous solution is successfully carried out in a flow sys-

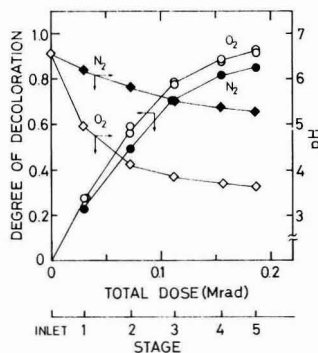
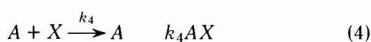
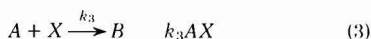
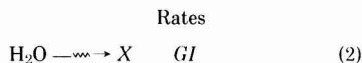


Figure 5. Degree of decoloration and pH at each column in nitrogen and oxygen bubbling systems
Solution feed rate, 5.0 L/min; inlet concentration of dye, 100 ppm; gas bubbling rate, 1.0 L/min; beam current, 2 mA

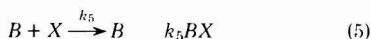
tem using a multistage, dual-tube bubbling column reactor. The decoloration is not affected by oxygen bubbling in the initial stage, but a slight difference appears in later stages, and the oxygen bubbling system gives a higher degree of decoloration than the nitrogen bubbling system. In oxygenation, 95% of the degree of decoloration is obtained by about 0.2 Mrad irradiation for 100 ppm inlet dye concentration. The pH changes with irradiation are affected significantly by DO. The decreases of the pH and the absorbances at 230 nm suggest that the dye degrades via formation of organic acids.

Reaction Scheme and Rate Expression of Decoloration.

According to Suzuki et al. (3), the main active species concerned with the decoloration of Acid Red 265 is the OH radical, and the G value for decoloration at the earlier stage of reaction is 1.0 molecule/100 eV. And the scheme of decoloration in the earlier stage is accepted as follows:



As the amount of decolored compound becomes nonnegligible with the progress of decoloration, Reaction 5 is added as a competitive reaction for OH radicals in this study



where A , B , and X represent overall colored, decolored materials, and OH radicals, respectively, and these in the rate expressions are their concentrations. I is the dose rate; k_3 , k_4 , and k_5 are rate constants for the overall colored and decolored compounds; and k_3 is reported to be $9.3 \pm 1.4 \times 10^9$ L/mol-s for Acid Red 265 (3). G is the specific rate of OH radical formation in the aqueous system, and is given by

$$G = 1.035 \times 10^{-3} G_i \text{ mol/L-Mrad} \quad (6)$$

where G_i is the G value of OH radical formation in radiolysis of water.

The rate of decoloration, r_A , is given by

$$r_A = -dA/dt = k_3 AX \quad (7)$$

Assuming steady state as to the radical concentration in Reactions 2-5 leads to

$$X = \frac{GI}{(k_3 + k_4)A + k_5 B} \quad (8)$$

where B is substantially equal to $A_0 - A$, and A_0 is the initial concentration of the dye. From Equations 7 and 8

$$r_A = pqGI \quad (9)$$

where

$$p = \frac{\alpha A}{\alpha A + (1 - \alpha)(A_0 - A)}$$

$$q = \frac{k_3}{k_3 + k_4}$$

$$\alpha = \frac{k_3 + k_4}{k_3 + k_4 + k_5}$$

p is the probability that the OH radical attacks colored materials, and q the probability that the decoloration occurs in this case, respectively. Since G values of the decoloration and OH radical formation are 1.0 and 2.7, q is 0.37 (1.0/2.7), and k_4 is obtained as 1.58×10^{10} L/mol-s.

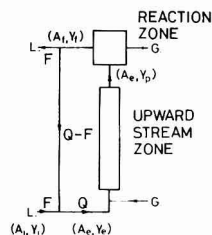


Figure 6. Schematic flow pattern in dual-tube bubbling column

Although $k_5(\alpha)$ is unknown, we carried out a parametric study to obtain the best fit values of α to experimental results at various reaction conditions.

Mass Balances in Dual-Tube Bubbling Column. The schematic flow pattern in the column can be assumed as drawn in Figure 6. The concentration of the dye in the reaction zone is given by Equations 10-13. In the downward stream zone, the decoloration is assumed negligible.

Reaction zone (complete mixing is assumed)

$$dA_f/dt = \frac{A_i - A_f}{\tau_r} - r_A = 0 \quad (10)$$

$$A_i = A_f/\nu + (1 - 1/\nu)A_f \quad (11)$$

$$r_A = \frac{\alpha A_f}{\alpha A_f + (1 - \alpha)(A_0 - A_f)} \quad (12)$$

$$\tau_r = V_r/Q$$

$$\nu = Q/F$$

where F and Q are the solution feed rate and the circulating flow rate in the column, and V_r is the volume of the reaction zone. Subscripts i , f , and e represent the column inlet, outlet, and upward stream zone inlet, respectively. For a multistage bubbling column reactor, A_f in a column is equal to A_i in the following column.

Comparison of Experiments and Calculations. Semi-logarithmic plots between $(1 - \eta)$ and total dose (corresponding to the number of the stage) for various solution feed rates are shown in Figure 7. In these experiments the optical density measured corresponds to A_i in Equation 10, as sampling is performed from the bottom of each column. The decoloration is not affected markedly by the feed rate, but slightly higher conversion is obtained for a higher flow rate. This is because backmixing is prevented, since more stages are needed to irradiate the solution by the same dose for the higher flow rate.

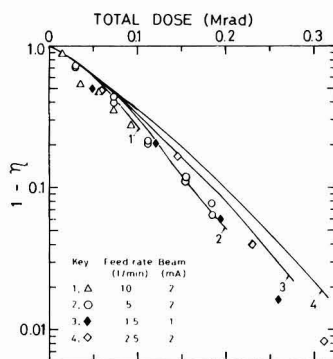


Figure 7. Effect of solution feed rate on decoloration. Inlet concentration of dye, 100 ppm; oxygen bubbling rate, 1.0 L/min; solid lines, calculated

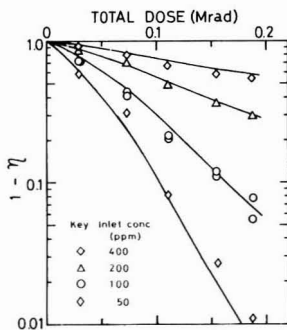


Figure 8. Effect of inlet concentration of dye on decoloration
Solution feed rate, 5.0 L/min; oxygen bubbling rate, 1.0 L/min; beam current, 2 mA; solid lines, calculated

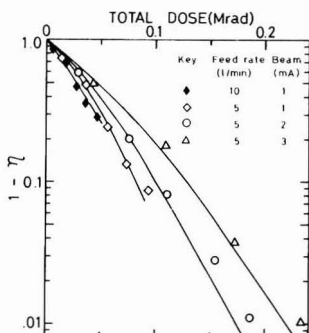


Figure 9. Effect of dose rate on decoloration
Inlet concentration of dye, 50 ppm; oxygen bubbling rate, 1.0 L/min; solid lines, calculated

Solid lines show the calculated values based on Equation 10 using 0.37 for q and 0.75 for α as the best fit value. The calculated values are tied by smoothed curves, although the values in the abscissa are essentially discontinuous ones. The agreement of calculations with experiments is fairly well except for the lower flow rate.

For the experiments for various inlet concentrations, $(1 - \eta)$ is plotted as a function of total dose in Figure 8. The calculated results agree well with the experiments for the range of the inlet concentrations from 50 to 400 ppm.

Figure 9 shows the relation between $(1 - \eta)$ and total dose at various dose rates. The lower dose rate gives a higher degree of decoloration for the same total dose because more stages are needed for the lower dose rate to irradiate by the same total dose. Good agreement between experiments and calculations was also obtained.

Figure 10 shows the results of various oxygen bubbling flow rates into the columns. At the later stages, slight differences in decoloration appear according to the bubbling flow rate; the higher conversion was for the higher bubbling rate. On the other hand, the calculations do not show such differences due to the bubbling rate because the effect of DO on decoloration is neglected in the calculation, although the decoloration seems to be slightly affected by DO for the later stages as seen in Figure 5.

DO Consumption with Irradiation. The DO concentrations in the reactor and upward stream zones are given by Equations 13 and 16. In the downward stream zone, the oxygen absorption is assumed negligible.

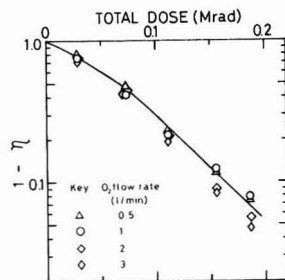


Figure 10. Effect of oxygen bubbling rate on decoloration
Solution feed rate, 5.0 L/min; inlet concentration of dye, 100 ppm; beam current, 2 mA; solid lines, calculated

Reaction zone:

$$\frac{dY_f}{dt} = \frac{Y_p - Y_f}{\tau_r} + K_{Lr}(Y_s - Y_f) - r_Y = 0 \quad (13)$$

Upward stream zone (backmixing is neglected)

$$dY/d\tau = K_{Lu}(Y_s - Y) \quad (14)$$

$$Y = Y_p \text{ at } \tau = 0$$

$$Y = Y_p \text{ at } \tau = \tau_u = V_u/Q$$

$$Y_c = Y_i/\nu + (1 - 1/\nu)Y_f \quad (15)$$

$$Y_p = Y_s - (Y_s - Y_c)e^{-K_{Lu}\tau_u} \quad (16)$$

where r_Y is the rate of DO consumption in the reaction zone, Y the concentration of DO, V_u the volume of the upward stream zone, and K_{Lr} and K_{Lu} are the overall capacity coefficients of oxygen absorption in the reaction and upward stream zones. Subscript p represents the upward stream zone outlet.

The second term on the right of Equation 13 can be neglected because the volume of the reaction zone is relatively smaller than that of the upward stream zone in this apparatus. The DO concentration in the reaction zone is derived from Equations 13–16 as follows:

$$Y_f/Y_s = 1 - \frac{\frac{1}{\nu} \left[1 - \frac{Y_i}{Y_s} \right] e^{-K_{Lu}\tau_u} + \frac{\tau_r}{Y_s} r_Y}{1 - \frac{\nu - 1}{\nu} e^{-K_{Lu}\tau_u}} \quad (17)$$

DO concentrations for various irradiation conditions are plotted in Figure 11 as a function of total dose. In this figure the DO concentration is expressed by the degree of saturation,

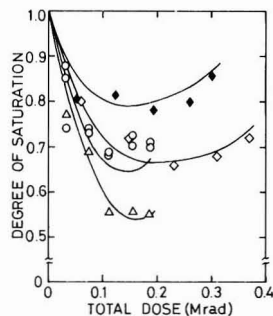


Figure 11. DO concentration in each column
Inlet concentration of dye, 100 ppm; solution feed rate (L/min); oxygen bubbling rate (L/min); beam current (mA): (♦) 1.5–1.0–1.0; (◇) 2.5–1.0–2.0; (○) 5.0–1.0–2.0; (Δ) 5.0–0.5–2.0; solid lines, calculated

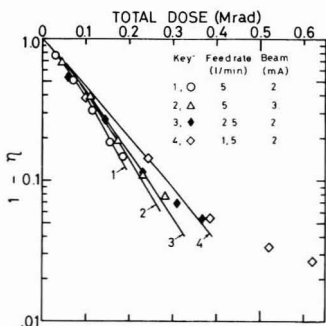


Figure 12. Decoloration of nitrogen bubbling solution
Inlet concentration of dye, 100 ppm; nitrogen bubbling rate, 1.0 L/min; solid lines, calculated

i.e., the ratio of DO concentration to the saturated one, Y_f/Y_s . The DO can be maintained at high concentration by using a reactor of this type for the high dose rate irradiation of electron beams, and the DO concentration decreases sharply in the initial stage and increases gradually in the later stages. The rate of oxygen consumption in the initial stage is indicated to be much higher than that of OH radical formation according to Equation 6. These facts indicate that colored materials consume more than one oxygen molecule when they are attacked by an OH radical, and that the rate of DO consumption decreases as the decoloration proceeds.

Decolored materials, on the other hand, may consume one oxygen molecule like most organics when they are attacked by an OH radical in the oxygen bubbling system. And organic radicals can be assumed to react with oxygen very fast. Based on these experimental results and assumptions on DO consumption, the rate of DO consumption is considered to be expressed as

$$r_Y = [\lambda p + (1 - p)]GI \quad (18)$$

where λ is the number of oxygen molecules consumed at the reaction of the colored material with OH radical.

To determine λ , a parametric study was performed according to Equations 17 and 18, and the value of λ was 3. The solid lines in Figure 11 show the calculated results.

Decoloration in Nitrogen Bubbling System. The results of irradiation of the nitrogen bubbling solution at various feed rates and beam currents are shown in Figure 12. Compared with Figure 7, the decoloration rate is smaller for the later stages. A parametric study was also performed to determine

α in a nitrogen bubbling system. The solid lines in Figure 12 show the calculated results using α of 0.63, but agreements with experiments are not good as seen in oxygen bubbling systems, especially in the later stages. α is smaller than that for the oxygen bubbling system; the reason is not clear, but the two cases may be considered. Firstly, decoloration may also occur by the oxidizing products formed by the degradation of the dye molecules in the oxygen bubbling system. Secondly, the decolored products in the nitrogen bubbling system may have a slight scavenging effect for the OH radical, that is, k_5 is larger than that for the oxygen bubbling system.

Appendix

When $\tau_r \ll \tau_u$ and $r_Y = 0$ (no irradiation) are assumed in Equation 17, K_{Lu} is given as

$$K_{Lu} = \frac{1}{\tau_u} \ln \left[1 + \frac{1}{\nu} \frac{Y_f - Y_i}{Y_s - Y_f} \right] \quad (19)$$

By measuring Y_i and Y_f of each column without irradiation, K_{Lu} can be calculated by using Equation 19.

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Empirical Insights into Lake Response to Nutrient Loadings, with Application to Models of Phosphorus in Lakes

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■ Data from 128 phosphorus limited lakes are used to determine the significance of various limnological parameters in models that allow the prediction of lake trophic state for given phosphorus loadings. A basic parameter used in the study is the steady-state concentration of a conservative substance in lakes (the average inflow concentration). By isolating this expression for phosphorus, the ability of various morphological parameters (hydraulic residence time, mean depth, surface area) to account for the nonconservative behavior of this nutrient is investigated. The data are first plotted on the phosphorus loading diagrams of Vollenweider and Dillon and then subjected to stepwise discriminant analysis. In each approach the residence time alone is statistically significant in describing the nonconservative behavior of phosphorus. The ability of residence time to replace Dillon's retention coefficient in predictive trophic state models and the advantages thereof are argued. Possible explanations for the significance of residence time are discussed.

Induced primarily by the activities of man, the cultural eutrophication of lakes has become over the last few decades a central issue of water pollution control. Concerned management agencies, theorizing that the rate of eutrophication can be consequently curbed if the input of nutrients to a water body is decreased, have expended large amounts of money for programs to reduce the flux of nutrients to lakes. Along with this management policy has come the need for a mathematical model able to assess the future trends of a given lake under a changing pattern of nutrient influx.

In this paper, data from a large number of lakes are used to determine the significance of various limnological parameters in simple nutrient budget models. Of primary concern are models that allow the prediction of lake trophic state once nutrient loadings are known. By isolating the expression for the concentration of a conservative substance in these models, the ability of various morphological parameters to describe the nonconservative behavior of nutrients is investigated. Because phosphorus is the limiting nutrient for most lakes in the temperate zone (1) and is of particular importance due to its relationship to man's activities, the study is restricted to this nutrient.

Existing phosphorus budget models and the respective loading diagrams are first examined. Conclusions extracted from this study are then substantiated by the multivariate statistical technique of stepwise discriminant analysis. Statistically significant parameter relationships pertinent to more complex deterministic phosphorus models are identified, and potential improvements in the analytical scope of predictive models of phosphorus in lakes are proposed. In addition, the resulting statistical functions are recommended as empirical predictive formulas of lake trophic state.

Data

The literature was searched for lakes sufficiently studied to provide the type of data necessary for the present analysis. A total of 128 lakes was found, including 71 eutrophic, 42 mesotrophic, and 15 oligotrophic lakes. (A complete listing of the data is available from the ACS Microfilm Depository Service.)

The European lakes investigated by Vollenweider (2), a group of Canadian lakes summarized by Dillon (3), the Great Lakes, and various other extensively studied lakes of the United States comprise the first 32 lakes. Additional data for these water bodies were found in Imboden (4) or Dunst et al. (5). All of the remaining lakes are located in the continental United States. Data for these 96 lakes were taken from the results of a National Eutrophication Survey conducted by the U.S. Environmental Protection Agency (6, 7). To ensure that the data selection remained unbiased, each lake that was phosphorus limited at the times of sampling with a mean depth of greater than 4 m was selected. Phosphorus limitation was established either by algal assay results or by the ratio of nitrogen to phosphorus concentrations.

The first 32 lakes have been extensively investigated, and as such the reliability of the reported data is adequate for models with large time scales of analysis. More caution must be exercised when using data for the other 96 lakes. Many of these lakes were sampled on only three occasions, and the estimated annual nutrient loadings were simply extrapolated from a limited number of grab samples. Previous studies of the respective water bodies by local interest groups were frequently used by the National Eutrophication Survey to enhance the reliability of the data.

One problem in the verification of models of trophic state is the subjective, nonstandardized procedures for designating the actual trophic state of a lake. A concise review of the methodologies used to classify the present 128 lakes is called for. In the case of the first 32 lakes, it is not obvious how the reported trophic states were assigned. Apparently, the classifications were based on a qualitative inspection of pertinent data for each lake. More specific guidelines were established for each of four key indicators to assign a trophic classification to the lakes of the National Eutrophication Survey (Table I). For cases in which all the parameter values did not fall within one trophic classification, a percentile ranking system was used. Details of this classification procedure are found in ref. 1.

Table I. National Eutrophication Survey Guidelines for Trophic State Determination [from Gakstatter et al. (1)]

Parameter	Oligotrophic	Mesotrophic	Eutrophic
Total phosphorus ($\mu\text{g/L}$)	<10	10–20	>20
Chlorophyll <i>a</i> ($\mu\text{g/L}$)	<4	4–10	>10
Secchi depth (m)	>3.7	2.0–3.7	<2.0
Hypolimnetic dissolved oxygen (% saturation)	>80	10–80	<10

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Table II. Simple Budget Models for Total Phosphorus

Investigators	Loss term	Steady-state phosphorus concn
Vollenweider	$\sigma AZ[\bar{P}]$	$[\bar{P}] = \frac{L_a\tau}{Z} \left(\frac{1}{1 + \sigma\tau} \right)$
Imboden; Snodgrass and O'Melia	$gA[\bar{P}]$	$[\bar{P}] = \frac{L_a\tau}{Z} \left(\frac{1}{1 + g\tau/Z} \right)$
Dillon	RL_aA	$[\bar{P}] = \frac{L_a\tau}{Z} (1 - R)$

Basic conservation of mass equation:

$$V \frac{d[\bar{P}]}{dt} = L_aA - q_sA[\bar{P}] - \text{Loss Term} (=0)$$

Background

Simple budget models for phosphorus in lakes represent a compromise between generality and reality. They are intended only to describe overall characteristics of phosphorus dynamics, and as such their direct use for prediction purposes is limited. On the other hand, because these models incorporate only simple relationships between a few common lake parameters, they are of value to the present study involving a large and diverse set of lakes.

Phosphorus in lakes is subject to chemical and biological transformations and transfer to (and from) the sediments. In simple mass balance models this "nonconservative" nature is incorporated into a loss term. Various expressions for the loss term have been proposed, each leading to a unique expression for the steady-state concentration of total phosphorus (Table II). Vollenweider (8) considers that phosphorus is removed by a first order reaction occurring throughout the lake. Imboden (4, 9) and Snodgrass and O'Melia (10) consider sedimentation as the principal removal mechanism and treat the loss as an output of phosphorus across the sediment-water interface only. Another approach is that of Dillon (3), who defines a retention coefficient as the fraction of incoming phosphorus that is lost by internal processes (e.g., sedimentation). Other investigators [Larsen and Mercier (11), Sonzogni et al. (12)] have formulated similar models, but these will not be considered further since their relationships are basically rearrangements of those of Dillon.

The last column of Table II gives the steady-state phosphorus concentration in a form that separates the conservative term, $L_a\tau/Z$ (the steady-state phosphorus concentration in the absence of internal losses), from the various expressions corresponding to the loss terms. In each expression the loss parameter is combined with parameters of lake morphology in a nondimensional quantity: $\sigma\tau, g\tau/Z, R$.

Early empirical studies of lake response to nutrient loadings have indicated that mean depth is the dominant morphological parameter [e.g., Rawson (13), Sakamoto (14)]. A similar conclusion can be drawn from the widely referenced phosphorus loading-mean depth diagram of Vollenweider (Figure 1). That is, for a given degree of eutrophy, deep lakes are capable of assimilating higher areal loadings of phosphorus than shallow ones. An examination of Vollenweider's expression in Table II indicates, however, that for a given concentration of phosphorus in the inflow ($L_a\tau/Z$), the mean annual phosphorus concentration is unrelated to mean depth if the parameter σ can be taken as a constant. A suitable explanation for the inverse relationship proposed by Vollenweider's diagram is simply the respective presence of areal loading and mean depth in the numerator and denominator of the $L_a\tau/Z$ term.

Snodgrass and O'Melia argue that the most cogent loss term is that of Imboden. The corresponding equation (second line

of Table II) implies that the phosphorus concentration is positively related to mean depth for a given inflow concentration if the sedimentation velocity (g) is reasonably constant. The use of the Imboden loss term in a more complex model likewise reversed the observed trend by predicting that deeper lakes will have higher phosphorus concentrations in their euphotic zones than shallow lakes (4, 9, 10). To resolve this discrepancy in their two-box model, Snodgrass and O'Melia have proposed to assign a depth dependence to the coefficient of exchange across the thermocline and to the effective settling velocity of the particulate phosphorus. The second of these functionalities is the most significant in allowing a good fit between observed phosphorus concentrations and those predicted by the two-box model of Snodgrass and O'Melia.

An outcome of Dillon's mass balance model (third line of Table II) is a critical phosphorus loading diagram for trophic state prediction akin to those of Vollenweider. However, a critical problem in using Dillon's formulation for predictive purposes is an inherent uncertainty when extrapolating a knowledge of present retention coefficients to the study of future loading effects. That is, due to chemical and biological interactions, the retention coefficient is itself dependent on the nutrient loading. Dillon himself notes a decreased phosphorus loading-higher retention coefficient trend (3).

If the mean annual phosphorus concentration $[\bar{P}]$ is a good indicator of trophic state (somewhat of a tautology in light of Table I), then conversely loading diagrams delineating trophic states must contain implicit information regarding the actual phosphorus concentration. In particular, it must be possible by analyzing such diagrams to decide whether the effect of mean depth on $[\bar{P}]$, and therefore on the trophic state of the lake, is simply that which appears in the conservative term, $L_a\tau/Z$, or if an effect of mean depth on the nonconservative behavior of phosphorus must be invoked to explain the data. A reexamination of phosphorus loading diagrams with an extended data base will answer this question.

Given limnological data on a large number of lakes, a more general objective is to decide what parameters are significant in the discrimination of trophic state. Conventional techniques for examining an extensive collection of data to study the significance of various parameters and their relationships are those of multivariate statistics. To date, only a few ap-

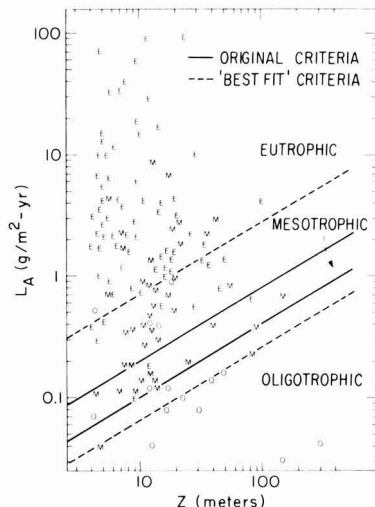


Figure 1. Areal phosphorus loading vs. mean depth diagram [after Vollenweider (2)]

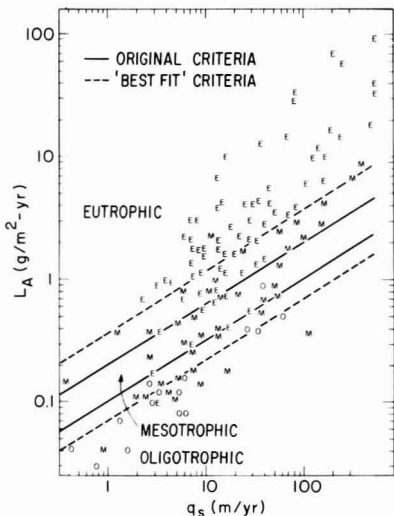


Figure 2. Areal phosphorus loading vs. hydraulic loading diagram [after Vollenweider (8)]

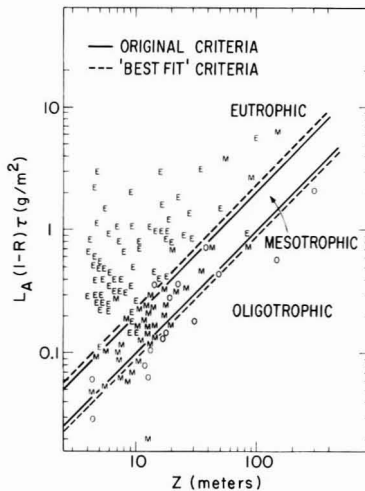


Figure 3. Dillon's parameter vs. mean depth diagram [after Dillon (3)]

plications of multivariate techniques to the study of lakes have been reported. Shannon and Brezonik (15, 16) classified the trophic state of 55 Florida lakes by cluster analysis using the trophic state indicators primary production, chlorophyll *a*, total phosphorus, total organic nitrogen, Secchi disc, specific conductivity, and Pearsall's cation ratio. To rank the lakes on a more quantitative basis, a trophic state index was derived by principal component analysis from the correlation matrices of the trophic indicators. A more recent and intriguing application is Boland's attempt to estimate lacustrine trophic state using multispectral scanner data from the satellite LANDSAT-1 (17). Included in this work is the application of principal component analysis to define a multivariate trophic state index based on indicators similar to those of Shannon and Brezonik.

While these applications of multivariate statistics will promote the standardization and quantification of the definition of trophic state, the present study is concerned with the statistical resolution of critical questions related to trophic state classification. For example, is the classification in three trophic states sufficiently precise to permit a clear identification of relative phosphorus concentrations, at least of the conservative term $L_a\tau/Z$? Can the analysis be pushed further and provide insights into the significant limnological parameters that govern the nonconservative behavior of phosphorus in lakes? In short, can guidelines for the development of cogent deterministic models for trophic state prediction be established?

New Look at Phosphorus Loading Diagrams

For purposes of this investigation, a straightforward method of quantifying the results of loading diagram studies is to plot pertinent data onto the diagrams and simply count the number of lakes that are positioned in the correct trophic level relative to the total number of lakes considered. This is done using data from the 128 lakes available to this study and the loading diagrams of Vollenweider (2, 8) and Dillon (3) (Figures 1-3). Two sets of lines demarcating the three trophic levels are shown in each figure. The solid lines are those presented in the original model formulations, while the dashed lines represent the set of parallel lines that optimizes the number of correct predictions for the present set of lakes.

Table III includes the results of this procedure, with the number of lakes correctly predicted for each group given as a percentage of the total number of lakes in the group. Also summarized in Table III are the results of a second procedure in which the regions defining each trophic level are simple intervals on a one-dimensional axis corresponding to a pertinent combination of the respective parameters. Note that while the total number of correctly predicted lakes is a reasonable indicator of the discriminating capability of each scheme, a comparable index is the percentage of correctly classified mesotrophic and oligotrophic lakes. This results from the fact that the areal phosphorus loading of eutrophic lakes is unbounded from above and numerous lakes with extremely high loadings are correctly classified no matter what

Table III. Results of Analysis of Phosphorus Loading Diagrams

Type of plot ^a	Percent of lakes predicted correctly												
	Original criteria				"Best fit" criteria				One-dimensional analysis				
	Total	E	M	O	Total	E	M	O	Parameter	Total	E	M	O
L_a, Z	69	96	26	60	73	83	64	53	L_a/Z	71	78	64	60
$L_a, q_s (= Z/\tau)$	70	89	31	93	76	74	76	80	$L_a\tau/Z$	77	91	65	33
$[L_a(1-R)\tau], Z$	78	95	55	67	82	92	73	60	$\frac{L_a(1-R)\tau}{Z}$	82	92	73	60

^a Retention coefficient (R) not available for six eutrophic and two mesotrophic lakes.

combination of parameters is considered. Mesotrophic and oligotrophic lakes are in a sense bounded, however, and the effects of other parameters on their classification are consequently more significant.

The first section of Table III reports the results based on the original criteria of Vollenweider and Dillon. It is interesting to note how biased the original models are to eutrophic lakes, and to a lesser degree oligotrophic lakes, at the expense of mesotrophic lakes. This is no doubt due to the small number of mesotrophic and oligotrophic lakes under study at that time. By reformulating the criteria as a "best fit" to the present set of data, both an increase in the total percentage of correctly predicted lakes and a definite reduction in the biased nature of the predictions are achieved. Dillon's diagram required a relatively small revision. Such a result supports the use of total phosphorus concentration as an indicator of trophic state, for the lines originally demarcating the three states in Dillon's diagram represent phosphorus concentrations of 10 and 20 $\mu\text{g/L}$. These same phosphorus levels, initially recommended as separators of trophic state by Sawyer (18), were used in the National Eutrophication Survey (Table I).

The importance of including the hydraulic residence time and the retention coefficient in trophic state classification schemes is indicated by the results of the "best fit" criteria (second section of Table III). The contribution of the hydraulic residence time is most notably reflected in a significant increase in the percentage of correctly classified mesotrophic and oligotrophic lakes, while Dillon's incorporation of a coefficient to account for the nonconservative behavior of phosphorus provides considerable improvement in the prediction reliability for the total set of lakes.

Of more concern to subsequent sections is a comparison of the results based on log-log plots of various parameters and those of a one-dimensional grouping of the same parameters (last two sections of Table III). Because of the log-log nature of the plots, the results of the two sections would be identical only if the slope of the demarcation lines is unity. Such is the case with Dillon's scheme (Figure 3).

The criteria lines for Vollenweider's original loading diagram have a slope of 0.6 (Figure 1). If this diagram is the optimum trophic state classification scheme that uses areal loading and mean depth, then the parameter $L_a/Z^{0.6}$ would provide the optimum separation in a one-dimensional analysis. However, the simple ratio L_a/Z (phosphorus loading per unit lake volume) does equally well. In other words, rather than some hidden nonlinear effect of mean depth on a lake's assimilative capacity, it is inferred that the apparent significance of mean depth in Vollenweider's treatise is simply a consequence of his use of areal loading rather than volume loading. Shannon and Brezonik (15) express the same notion by excluding both areal loading and mean depth in favor of volume loading in their regression analysis of a trophic state index.

Consider next Vollenweider's second generation phosphorus loading diagram (Figure 2), upon which the hydraulic loading rate (mean depth/residence time) replaces the mean depth as the critical morphological parameter. The slope of the demarcation lines is 0.5, indicating that the parameter $L_a(\tau/Z)^{0.5}$ is an excellent one-dimensional discriminator of lake trophic state. A more fundamental, dimensionless quantity formed by the component parameters is $L_a\tau/Z$, the steady-state concentration of a conservative substance in a lake. The discrimination achieved by this concentration term is unsatisfactory, however, due to the low percentage of correctly classified mesotrophic and oligotrophic lakes. That the nonconservative nature of phosphorus must be incorporated into a trophic state classification scheme is a logical conclusion. Of more interest is an indication that the term $(\tau/Z)^{0.5}$ is effective in progressing from a "poor" to a "good" classifi-

cation scheme. In some complex way, this term is able to reflect the internal loss of phosphorus. Whereas the use of the hydraulic loading makes it impossible to separate the effects of mean depth and residence time, the previous analysis has disclosed no anomalous effects of mean depth on a lake's response to phosphorus loading. It follows that the hydraulic residence time must be the critical parameter. In the next section, this conclusion is substantiated through the use of multivariate statistics, which enables an isolation of the contributions of mean depth and residence time to trophic state prediction.

Stepwise Discriminant Analysis Applied to Predictive Models for Lakes

Discriminant analysis is a multivariate statistical method that allows the classification of a multidimensional observation vector into one of several multivariate normal populations. Because not all of the observed variables are needed to discriminate between the populations in many cases, a modified procedure has been formulated to identify the subset of these variables that furnishes the "best" discrimination. This is the method of stepwise discriminant analysis. As applied to this study of the degree of eutrophy of lakes, the three trophic states are the "populations", and the observed "variables" include mean depth (Z), hydraulic residence time (τ), surface area (A), phosphorus retention coefficient (R), and mean annual phosphorus loading per unit surface area (L_a). The primary goal is to be able to classify a lake into a certain trophic state once its variables are known. A more specific purpose for this application of the stepwise procedure is to clarify the position of various lake parameters in trophic state identification.

The stepwise discriminant analysis program used for this study was BMD 07M (19). The logic of the stepwise procedure is analogous to that of stepwise multiple regression and is presented in detail by Afifi and Azen (20). For purposes of this study, the procedure can be sufficiently summarized by referring to Table IV. The first two columns merely identify the case number and the combination of limnological variables selected for analysis. The third column lists these variables in the order in which they have entered the discriminating set. The variable entered at each step is that for which an F statistic based on a one-way analysis of variance test is maximum. This statistic (F' in column 4) is a measure of the "difference" in the mean values of the conditional distributions of the populations for each variable, given the variables already entered. Column 5 gives the tabulated values of the F -distribution for the 95% significance level. The hypothesis that the entering variable significantly contributes to the discrimination between populations is rejected at a prescribed significance level if F' is less than the value of the F distribution at that level.

After the last step of each case, the output of the program includes the coefficients of the canonical variables and a scatter diagram of trophic state discrimination based on the first and second canonical variables. Canonical variables are linear combinations of the limnological parameters and can be used to advantage because the first one or two often explain most of the variance in the multidimensional cloud of data points. The value of canonical variables to the present study is discussed below.

For each case, input to the stepwise discriminant analysis program includes the number of lakes in each of the three trophic states and the values of the selected parameters for each lake. To satisfy the assumption of normality, a transformation of the data to the logarithmic scale is required. Numerous combinations of the parameters were tested. Four are considered here (Table IV).

Table IV. Summary Table for Stepwise Discriminant Analysis

Case	Variables considered	Variable entered	F'	F _{0.95} (ν ₁ , ν ₂) ^a
1	L _a , Z, τ, A	L _a	46.71	3.07
		Z	3.65	3.08
		τ	19.31	3.08
		A	0.52	3.08
2	$\frac{L_a\tau}{Z}$, Z, τ, A	L _a τ/Z	40.64	3.07
		τ	29.32	3.08
		A	0.56	3.08
		Z	0.02	3.08
3	$\frac{L_a(1-R)\tau}{Z}$, Z, τ, A, (1-R)	L _a (1-R)τ/Z	78.22	3.07
		τ	8.43	3.08
		(1-R)	4.33	3.08
		A	1.36	3.08
		Z	0.07	3.08
4	$\frac{L_a(1-R)\tau}{Z}$, Z, A, (1-R)	L _a (1-R)τ/Z	78.22	3.07
		1-R	1.11	3.08
		Z	1.65	3.08
		A	0.56	3.08

^a ν₁ = G - 1; ν₂ = N - G - V (G = number of groups; N = total number of lakes; V = number of variables entered).

Case 1 considers the four fundamental independent parameters. It is determined that surface area is not a significant discriminatory variable. This is not surprising since the loading term has already been normalized by the surface area. A second finding is that areal loading and mean depth contributions are not fully realized until the residence time is included, as evidenced by the high F' value for residence time once the other parameters have entered. (A considerable 17% increase in the total number of correctly predicted lakes accompanied the inclusion of residence time.) The presence of L_a, Z, and τ in this classification scheme allows a comparison with the results shown in the second line of Table III. Of primary interest is the first canonical variable for case 1:

$$CV(1) = 2.98 \log L_a + 1.88 \log \tau - 2.85 \log Z + 3.19 \quad (1)$$

$$CV(1) \approx 2.98 \log \{L_a\tau/Z\} - 1.10 \log \tau + 3.19 \quad (2)$$

This canonical variable accounts for over 98% of the total dispersion of the present data; thus, it can serve as a reliable one-dimensional scheme for trophic state classification. The only governing parameter other than the "conservative" phosphorus concentration (L_aτ/Z) is the hydraulic residence time, thereby supporting the conclusion that it is highly correlated with in-lake phosphorus losses. For a given value of L_aτ/Z, lakes with larger residence times cause a lower value of CV(1) indicative of better lake conditions. A higher phosphorus retention also implies more desirable conditions. It follows that the correlation between residence time and phosphorus retention is positive.

That the residence time is statistically the only morphological parameter effective in describing the nonconservative behavior of phosphorus is even more apparent in case 2. Not only does the large F' value for residence time indicate its great significance, but the exceptionally low F' values for mean depth and surface area discredit their role in the regulation of phosphorus losses.

Dillon's use of a measured retention coefficient should be sufficient to account for phosphorus losses under current loading conditions. The corresponding parameter for average phosphorus concentration, L_aτ(1-R)/Z, is included in case 3 to test its discriminating capacity. The residence time (τ)

remains significant over and above its inclusion in the concentration term. It is also determined that (1-R) is significant, but the results of case 4 reveal no such significance when residence time is excluded. The presence of (1-R) in case 3 reflects a counterbalance to the highly correlated residence time. One possible explanation for the independent appearance of τ as a significant discriminator is that measured phosphorus concentrations are commonly spring or summer values, whereas the concentration defined by Dillon's model is an annual average. The statistical routine discriminates between trophic states defined by the former. Some phenomena affected by this temporal difference, as for example thermal stratification, may be accounted for by the presence of residence time.

The high correlation between residence time and the retention coefficient is very attractive to simple predictive models of lake trophic state. As discussed earlier, the apparent success of any classification scheme involving R is diminished in that this coefficient, as defined, is not determinable under changing loading conditions until the new phosphorus budget is known. It is now proposed that two known parameters, L_aτ/Z and τ, are sufficient to predict a priori the trophic state of a lake. The prediction accuracy of the classification functions of case 2 is equivalent to that using Dillon's parameter in case 3. These classification functions, updated to exclude the effects of erroneously classified lakes, are given in Table V. Given the variables for an "unknown" lake, its classified trophic state is that for which the classification function is a maximum.

Discussion of Results

The significance of the term L_aτ/Z in the discrimination of lake trophic state is expected in that it is the average concentration of phosphorus in the inflow. A somewhat unforeseen result is that for the morphological parameters considered, the hydraulic residence time alone is statistically significant in describing the nonconservative behavior of phosphorus in simple deterministic trophic state models. Several processes affecting the distribution of phosphorus in lakes entail coefficients that can be nondimensionalized by the residence time. These include phosphorus settling, first-order

Table V. Classification Functions for Proposed Trophic State Classification Scheme

Trophic state	Classification functions
Eutrophic	$F(E) = -12.542 \log \left(\frac{L_a \tau}{Z} \right) + 1.648 \log (\tau) - 5.889$
Mesotrophic	$F(M) = -25.063 \log \left(\frac{L_a \tau}{Z} \right) + 5.146 \log (\tau) - 18.873$
Oligotrophic	$F(O) = -31.475 \log \left(\frac{L_a \tau}{Z} \right) + 9.130 \log (\tau) - 30.009$

reactions, and lake mixing. Data limitations prohibit an investigation of the relative significance of each process through discriminant analysis. Each is now briefly discussed.

Imboden and Snodgrass and O'Melia express the mean annual phosphorus concentration as (Table II):

$$[\bar{P}] = \frac{(L_a \tau / Z)}{1 + (g \tau / Z)} \quad (3)$$

Assuming that this concentration is a satisfactory indicator of trophic state, it follows that the conspicuous presence of the residence time in the previous analyses must be reflected in the dimensionless settling term, $g\tau/Z$. A consequence is the repudiation of the use of a constant settling velocity for all lakes in simple models, for if the velocity term (g) is constant the significant parameter is the ratio of residence time and depth. Both the loading diagram analysis and the stepwise discriminant analysis have invalidated such a significance. The dominance of a settling process can be maintained, however, if one of two conditions is satisfied. First, if the velocity term is directly dependent on mean depth so that g/Z tends to a scalar, then only residence time remains. Snodgrass and O'Melia have used flocculation arguments to derive such a relationship for hypolimnetic settling (10). A second possibility is to consider the appropriate depth scale (Z) to be a parameter that is quasi-constant for all lakes (or at least somewhat uncorrelated to other morphological parameters). An example is the thickness of the epilimnion. However, Snodgrass and O'Melia found that predicted phosphorus concentrations are quite insensitive to the epilimnetic settling rate.

One can also postulate that a first-order reaction (e.g., phosphorus mineralization) is the dominant process governing phosphorus distribution. A term of the form $\sigma\tau$ would be required in the denominator of Equation 3, thereby justifying to some extent Vollenweider's original conception (Table II). From a dimensionless parameter standpoint, the importance of residence time independent of other morphological parameters is explainable only if the rate coefficient (σ) satisfies this independence. For reactions of a chemical or biological nature this is a credible assumption. The previously discussed two-box model of Snodgrass and O'Melia considers a reversible chemical-biological reaction between dissolved orthophosphate and "particulate" phosphorus. If a new phosphorus compartment representing the mineralized form is introduced, so that its reconversion to orthophosphate is prohibited, the associated rate coefficient would impart added significance to the residence time. It is conceivable that the observed relationship between the assimilative capacity of a lake and its mean depth results indirectly from the high correlation between depth and residence time. Snodgrass and O'Melia's use of two depth-dependent processes to moderate their predictions, discredited by the present findings that depth effects are insignificant, may not be necessary.

One final process affecting phosphorus dynamics that can be used to normalize the residence time is vertical mixing. Snodgrass and O'Melia (10) and Stauffer and Lee (21) are among those who have recognized the importance of the ex-

change of nutrients across the thermocline during the stratification season.

A somewhat unrelated interpretation of the present result, that lakes with longer residence times exhibit better trophic conditions, is that such lakes have not yet "caught up" with historically increasing concentrations of phosphorus in the inflow ($L_a \tau / Z$). A basic assumption of the present empirical study is that the lakes are at steady-state under the reported phosphorus loadings. This is not entirely satisfied in most cases. To test the hypothesis that the importance of residence time is due to the slow response time of some lakes relative to historical increases in phosphorus loading, case 2 of the stepwise discriminant analysis has been repeated excluding all lakes with residence times greater than five years. The F' value for the residence time (entered after $L_a \tau / Z$) remains highly significant even though it is reduced from 29.32 to 9.46, indicating that the equilibration time hypothesis is not sufficient to totally explain the significance of the hydraulic residence time.

Concluding Remarks

An attempt has been made in this paper to advance the modeling of lake response to nutrient loadings, especially phosphorus. Utilizing data from 128 lakes, existing phosphorus loading diagrams are reexamined, and the multivariate technique of stepwise discriminant analysis is applied. Both methods of data analysis produce a "model" capable of lake trophic state prediction.

The science of limnology has progressed beyond such an "empirical" modeling stage, however, and modifications that advance the applicability of simple lake models are called for. The interfacing of simple phosphorus models with existing chemical and hydrodynamic models potentially provides a better definition of the speciation of phosphorus and its concurrent transport due to physical processes (22). What is critical is that observed, basic trends must continue to be satisfied as model complexity increases. This study has identified such a trend: that the hydraulic residence time and the assimilative capacity of a lake are positively correlated. Though the empirical approach prohibits the identification of a "causal" relationship, the statistical significance is clearly demonstrated.

Acknowledgment

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Nomenclature

A = surface area of a lake, L^2
 E = "eutrophic" (classified trophic state of a lake)
 F' = F statistic based on a one-way analysis of variance test

g = sedimentation coefficient, L/T
 L_a = annual phosphorus loading per unit lake surface area, $M/L^2 \cdot T$
 M = "mesotrophic" (classified trophic state of a lake)
 O = "oligotrophic" (classified trophic state of a lake)
 q_s = hydraulic loading rate (areal rate of total water inflow), L/T
 R = phosphorus retention coefficient
 V = volume of a lake, L^3
 Z = mean lake depth, L
 $[\bar{P}]$ = steady-state concentration of total phosphorus, M/L^3
 σ = volumetric sedimentation coefficient, T^{-1}
 τ = hydraulic residence time of a lake, T

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Supplementary Material Available. A complete listing of the lake data (5 pages of tabular material showing lake, location, trophic state, mean depth, hydraulic loading rate, areal phosphorus loading, and retention coefficient) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Operations Office, Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number ES&T-78-195.

Industrialization of New Haven, Conn., as Recorded in Reservoir Sediments

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■ The industrialization of New Haven, Conn., has resulted in increased fluxes of Ag, Cd, Cu, Ni, Pb, V, and Zn to the sediment as compared to preindustrialization fluxes. Pb is primarily derived from lead tetraethyl in gasolines and Cu from CuSO₄ added as a biocide to the reservoirs. Fossil fuel burning is not a significant source for the metals in the reservoir sediments.

The technologically advanced areas are having an ever-increasing effect upon the sediments being deposited in their vicinity. More industrial and agricultural by-products are being added to air and water and hence to reservoirs, lakes, and oceans where they may be incorporated into the modern sedimentary record. A history of man's influence upon the environment can be interpreted through an analysis of the heavy metal chemistry of these sediments (1).

Ideal localities for this purpose are areas of anoxic sedimentation that are hostile environments for most organisms. Therefore, bioturbation of the sediment is minimal, and the depositional record is not measurably disturbed. Sediment cores should penetrate deeply enough to sample material unaffected by man's presence in order to measure the natural metal background levels established by weathering processes.

The city of New Haven, Conn., had a 1970 population of 138 000 (New Haven County population was 744 948) (2) (Figure 1). The area developed as an industrial center in the 1800's. Its suburbs (East Haven and Hamden) underwent rapid expansion after World War II. Metal fabrication and finishing, brass manufacturing, and arms manufacturing plants were established, and many are still functioning today. The main electric power generator of the region (United Illuminating) is situated in downtown New Haven. A highly developed network of highways is spread throughout the region. All are potential sources of metals in the reservoir sediments. This study was designed to assess their impact upon the makeup of sediments and to evaluate the relative contri-

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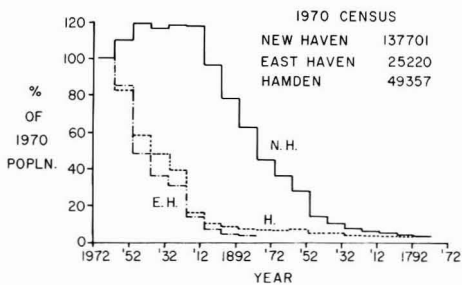


Figure 1. Population trends of New Haven, East Haven, and Hamden, Conn.

butions for any metal from a given source.

Two reservoirs were studied. Lake Whitney and Lake Saltonstall are situated near New Haven, 8 km apart, and are on different drainage systems. Lake Whitney is located 4 km north of downtown New Haven, whereas Lake Saltonstall is located 6.4 km east of New Haven (Figure 2). Storm drainage from Whitney Avenue, a major thoroughfare to downtown New Haven, empties directly into Lake Whitney. Lake Saltonstall is essentially free from storm drainage. There are no known instances of industrial pollution by the direct discharge of wastes into the drainage systems of either Lake Whitney or Lake Saltonstall.

On June 6, 1975, two cores were taken by divers from the bottom sediments of both reservoirs, frozen, and then shipped to San Diego, Calif., for analysis.

Lake Whitney (Figure 2) was originally a wide portion of the Mill River and was first dammed in the 1700's. Its dam was raised in 1860 to its present level. This reservoir has a storage capacity of approximately 977 million L extending over 0.72 km². It receives drainage from 26 sq km of land. The Lake Whitney core (57 cm long) was taken from a location immediately upstream of the dam (41°20'08"N; 72°54'52"W) in approximately 6 m of water.

The Lake Saltonstall core (63 cm long) was taken in 20 m of water (41°17'51"N; 72°50'50"W). The lake was formed during the last glacial advance and had an original watershed area of 13 sq km. In 1901 the reservoir's drainage area was enlarged by diverting the nearby Farm River through a 3.22-km tunnel into the lake. This raised the total watershed area to 39 sq km. The lake covers 1.6 sq km and holds 5.7 million L.

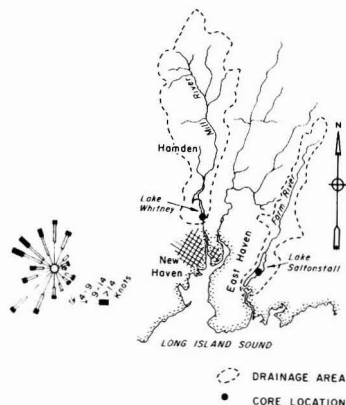


Figure 2. Location map of Lake Whitney and Lake Saltonstall. Average wind direction and speed in New Haven, Conn.

Prior to the dissection of the cores, slabbed sections were x rayed. The Lake Whitney core had visible layers of 0.5–1.0 cm thickness to a depth of 50 cm. Below 50 cm the bedding disappeared, and the sediment contained a much greater percentage of plant material. The core was sampled at 1-cm intervals.

The Lake Saltonstall core had some visible fine layering in the black, upper 13.6 cm of sediment. Below this black layer was a zone of red-brown sediment 16.4 cm thick that graded into darker brown laminations at 30 cm and continued to the bottom of the core. Red-brown sediment (representative of oxidizing conditions) underlying black sediment (anoxic conditions) is uncommon in the recent sedimentary record. The possibility of the black sediment resulting from changed conditions after the tunnel construction in 1901 was considered. If this were the case, it would indicate a sedimentation rate of about 0.2 cm/year. Therefore, smaller sampling intervals would be required to reveal changes in the more recent years. Samples were taken at about 0.5-cm intervals for the upper 14 cm; 1.0-cm increments from 14 to 40 cm; and at 2-cm increments from 40 to 63 cm.

Ages for the different levels in the cores were determined by the Pb-210 dating technique (3). Measurements of Al, Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn concentrations were conducted by atomic absorption analysis on the dissolved total sediment samples using a Varian (Model AA-6) atomic absorption unit with a background corrector for wavelengths under 3000 Å. The samples were ground, HCl leached, treated with HF, and wet-ashed (alternating HNO₃ and HClO₄) to totally put them into solution.

Using the concentrations of these elements at different levels (ages) in the sediment record, the sedimentation rates determined by Pb-210 and the density of the sediments, the natural heavy metal fluxes, and the anthropogenic metal fluxes in the sediment were calculated.

The amount of opal in the samples was determined by the method of Goldberg (4). Elemental carbon was determined by the method of Smith et al. (5).

Direction in identifying the major sources of the metals in the sediments resulted from measuring the isotopic ratios of lead. Chow et al. (6) have shown that lead ratios in sediments have changed as a consequence of man's utilization of lead alkyl additives in gasoline.

Results and Discussion

Sedimentation Rates. Lake Whitney accumulated sediment (Figure 3) at an average rate of 0.26 cm/yr up to 1950 on the basis of the Pb-210 activities. From 1950 to the present, this rate increased to 1.0 cm/yr coinciding with the post World War II building boom that occurred in the Mill River area (2) (Figure 1) and the opening of sand and gravel pits along the Mill River. Using these rates, the "peat"-sediment transition at 50 cm in the core dates as occurring in the late 1850's. This is in reasonable agreement with the raising of the dam in 1860. Prior to the damming, much of Lake Whitney was marsh land.

The Lake Saltonstall sedimentation rate changed from 0.14 cm/yr below 9 cm to 0.39 cm/yr in the upper 9 cm (Figure 4). The change in sedimentation rate occurred about 1953, agreeing with the post World War II building boom in East Haven. The black to brown color boundary at 13.6 cm would then have occurred in 1917. Considering that it probably took several years before the lake became anaerobic, the date is in reasonable agreement with the 1901 diversion of the Farm River into Lake Saltonstall.

Lake Whitney and Lake Saltonstall exhibit fourfold and threefold increases, respectively, in their sedimentation rates coincident with rapidly growing populations in their suburbs. At least part of these increased sedimentation rates is due to

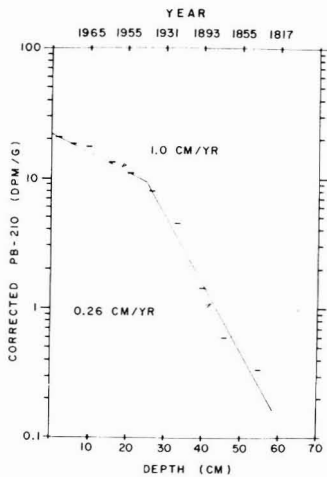


Figure 3. Corrected Pb-210 activity with depth in Lake Whitney sediments

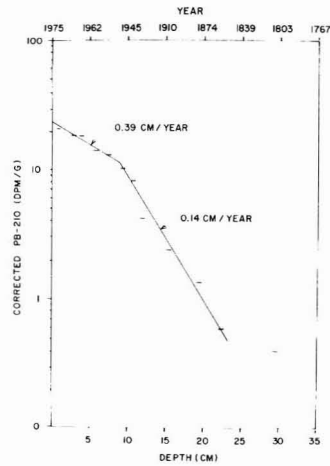


Figure 4. Corrected Pb-210 activity with depth in Lake Saltonstall sediments

increased biological productivity in the reservoirs in more recent times (Table I) as measured by the CaCO_3 and opal contents of the deposits. It is unlikely that dissolution of opal with depth, as suggested by Parker and Edgington (7) produced the opal pattern observed in the two lakes since the CuSO_4 requirement (based on clogging of water intake filters) shows the same pattern of biological productivity. Thus, urbanization of New Haven suburbs has greatly affected particle transport and biological productivity, which has resulted in decreased lengths of time their reservoirs are usable before silting up.

Metal Accumulations. Since the biological productivity of the reservoirs has changed with time, absolute concentrations of metals in the sediments are inadequate for discerning changes in heavy metal fluxes. Al is considered to reflect weathering processes. Fluctuations in the Al contents with depth usually reflect variations in biogenic content. By normalizing the metal concentrations to a constant Al concentration,

one obtains a representation of the nonbiogenic metal fluctuations in the sediments.

The concentrations for Ag, Pb, Cd, Cu, Ni, Zn, and V (normalized to constant Al content) exhibit similar patterns in Lake Saltonstall sediments (Figure 5) with higher concentrations in the more recent strata compared to the older strata. Fe and Mn have a maximum in their concentration between 7 and 9 cm (about 1950). Co and Cr concentrations remain essentially constant with depth.

The Al normalized metal patterns in Lake Whitney are more complex (Figure 6) with concentration maxima occurring between 1930–1953 for Ni and Zn, about 1962 for V and Cu, and 1965 for Pb, Fe, Mn, Co, and Ag concentrations are essentially constant with depth. Cr increases slightly in more recent times.

Natural or background fluxes and anthropogenic fluxes were calculated for the various metals in Lake Whitney and Lake Saltonstall sediments. Table II gives the natural fluxes, 1975 anthropogenic fluxes, and maximum anthropogenic fluxes for the elements. The natural fluxes for Lake Saltonstall were calculated using the metal concentration that accumulated after the tunnel completion date because the sediments were from a different source area. The natural fluxes for Lake Whitney were calculated from metal concentrations in the sediments just about the "peat" layer. These ratios may include some anthropogenic component since the Whitney Armory (later the Winchester Repeating Arms Co.) was located at the site of the dam since the early 1800's. In the late 1800's the arms company was one of the largest producers of cartridges in the United States and utilized brass (Cu, Zn) for the shell casings and lead for the bullets. A comparison of the natural fluxes of Lake Whitney and Lake Saltonstall shows that the natural fluxes of Pb, Zn, Cd, and Cu are higher in Lake Whitney by about a factor of three to four (more than the difference in sedimentation rates, 2.4) and probably reflects the cartridge manufacturing.

The 1975 anthropogenic metal fluxes for Pb, Cr, Ni, and V are more than an order of magnitude higher in sediments from Lake Whitney than in sediments from Lake Saltonstall. Zn and Ag have slightly higher anthropogenic fluxes in Lake Whitney than in sediments from Lake Saltonstall.

Metal Sources

Fossil Fuel Burning. Bertine and Goldberg (8) suggested that fossil fuel burning could mobilize many elements, par-

Table I. Biologic and Elemental Carbon Fluxes to Lake Whitney and Lake Saltonstall Sediments ($\text{mg}/\text{cm}^2/\text{year}$)

Sample (cm)	Org C	Elem C	CaCO_3	Opal
Lake Whitney				
6-7	2.1		2.5	2.6
7-9		0.7		
11-12		0.8		
12-13	2.1		2.1	6.6
18-19		1.3		
19-20	2.3		2.0	5.6
27-28	0.9	0.6	0.2	2.2
32-33	0.7		0.4	1.3
36-37		0.3		
38-39	0.7			0.8
46-47	0.9	≤ 0.1	0.1	1.0
55-56	0.6		0.4	0.4
Lake Saltonstall				
2.5-3.2	0.6		0.5	2.4
5.3-6.2	0.5		0.3	2.3
7.1-7.8	0.5		0.2	1.8
10.3-11.0	0.2		0.2	1.4
22-23	0.2		0.3	1.3
29-30	0.3		0.0	0.9
38-39	0.4		0.1	0.5
52-54	0.7		0.3	1.0

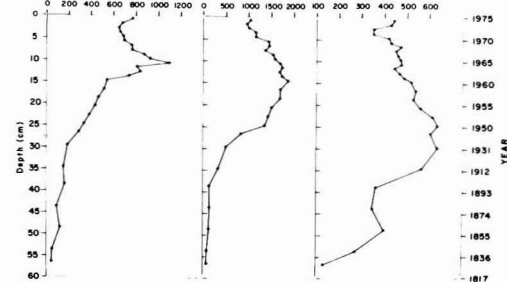
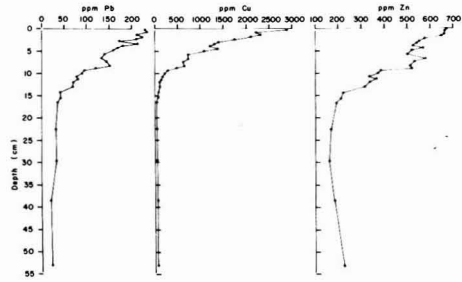
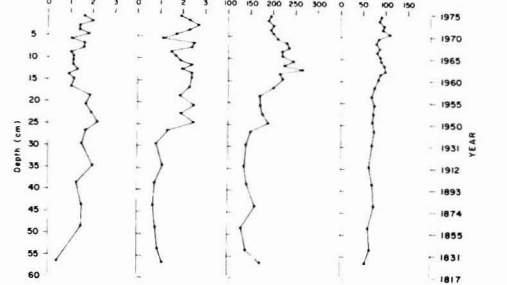
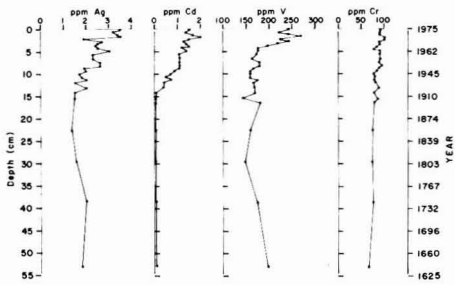
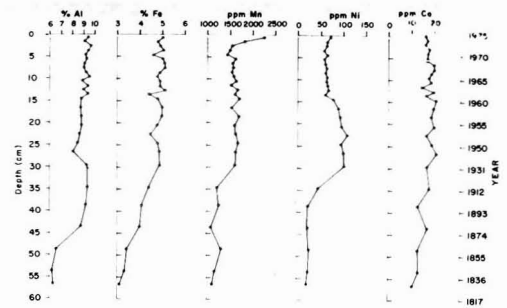
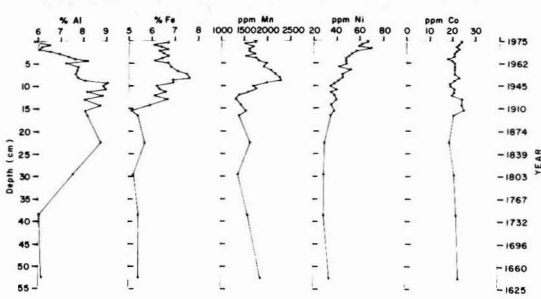


Figure 5. Al content and normalized metal concentrations with depth in Lake Saltonstall sediments

All elements except Al are normalized to Al content of 8.06% at 12.4–13.6 cm depth

Figure 6. Al content and normalized metal concentrations with depth in Lake Whitney sediments

All elements except Al are normalized to Al content of 8.80% at 43–44 cm depth

Table II. Comparison of Metal Fluxes to Lake Whitney and Lake Saltonstall Sediments with Metal Fluxes Emanating from Fossil Fuel Burning and CuSO₄ Additions (μg/cm²/year)

	Ag	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Lake Whitney											
Natural	0.18	0.08	2.0	8.5	16	4752	137	2.7	11	17	42
1975 Anthropogenic	0.07	0.43	...	7.9	329	4422	429	17	238	22	39
Max anthropogenic ^a	0.23	0.43	...	14	614	...	429	27	330	51	86
	(1950–1)	(1975)	...	(1970–1)	(1961–2)	...	(1975)	(1952–3)	(1964–5)	(1962–3)	(1950)
Lake Saltonstall											
Natural	0.10	0.02	1.1	4.3	5.6	3320	66	2.0	3.3	8.4	15
1975 Anthropogenic	0.06	0.07	164	0.8	8.3	1.0	15
Max anthropogenic ^a	0.06	0.09	...	0.3	164	880	77	0.8	9.8	3.1	22
	(1974–5)	(1970–1)	...	(1947–52)	(1974–5)	(1947–52)	(1952–3)	(1974–5)	(1966–7)	(1969–70)	(1963–4)
United Illuminating											
Coal (1957)	...	0.045	0.1	1.2	0.4	1020	1.0	0.8	0.4	2.9	6.6
Oil (1975)	...	0.00008	...	0.002	...	0.002	0.0008	0.08	...	0.4	0.0002
Copper from CuSO ₄											
Lake Whitney (1961–2)	480										
Lake Saltonstall (1971–2)	234										

^aYear of maximum.

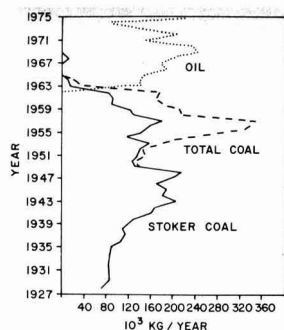


Figure 7. Coal and oil burned at United Illuminating power generating station, New Haven, Conn.

ticularly the more volatile ones, in amounts rivaling those of natural weathering processes. Klein et al. (9), Natusch et al. (10), and Kaakinen et al. (11) determined the pathways of many metals through coal-fired power plants. They found that As, Sb, Pb, Se, Tl, Zn, Hg, Cu, Ga, and Mo were more concentrated in the effluent compared to the bottom ash. In addition, higher concentrations of these metals were contained in the very small fly ash particles that were not collected by the electrostatic precipitators installed in the stacks. It is thought that these metals volatilize in the combustion zone but condense and/or become absorbed on the fly ash as the flue gas cools. Due to the increased surface area of the smaller particles, the metals become associated with the finest particles. Co, Mn, Fe, and Al remain in the solid phase. They are effectively removed in the bottom ash and by the electrostatic precipitators. Cr, Ni, and V exhibit intermediate behavior.

United Illuminating is the primary electricity generator in the New Haven area. Coal was burned in the United Illuminating power plant up to 1963 at which time the plant changed to number 6 oil. Prior to 1948 the coal was used in underfed stokers and pulverized firing boilers. Two out of five stacks were fitted with electrostatic precipitators. The total amounts of coal and oil burned since 1928 and the amount burned in the underfed stokers without the electrostatic precipitators are shown in Figure 7 (data supplied by United Illuminating). Data prior to 1928 are not available.

The coal burned by United Illuminating ranged between 7 and 8% ash. Stoker coal produces equal amounts of fly ash and bottom ash; pulverized coal produces 90% fly ash (9). The electrostatic precipitator is assumed to remove 90% of the fly ash (9). To calculate metal fluxes from coal and oil burning at United Illuminating, the concentrations of the metals in the inlet and outlet fly ash of Klein et al. (9) and the concentrations of the metals in the oils of Bertine and Goldberg (8) were used. Klein and Russell (12) reported that most of the increased metal concentrations in the soil around a coal burning plant in Michigan occurred within 11 km of the plant. The fallout pattern was highly dependent upon the wind speed and direction. Northerly and westerly winds are predominant in the New Haven area as shown by the wind rosette in Figure 2.

For calculation of the metal fluxes from the United Illuminating plant, all metals associated with the fly ash are assumed to fall out evenly over two-thirds of a circle with an 11-km radius. The results of these calculations for 1957 (maximum coal burning) and 1975 (oil burning) are compared to anthropogenic metal fluxes in the sediments in Table II. For most metals, coal burning was a more significant source.

Lake Saltonstall lies in a frequent downwind direction from the United Illuminating plant. Comparison of the anthropo-

genic metal fluxes in the sediments with those from coal burning indicates that most of the Cr, Ni, V, and Fe and about half of the Zn and Cd could have resulted from the coal burning. However, the pattern of ever-increasing concentrations in the sediments in recent times does not reflect the pattern that would have been produced if coal burning at the United Illuminating plant were the main source (Figure 7).

Lake Whitney is located to the north-northwest of the United Illuminating power plant. From the infrequency of winds in that direction, the influence of the power plant on the sediment composition is probably minor. Comparisons of the fluxes (Table II) also indicate that metal fluxes from United Illuminating are insignificant in Lake Whitney sediments.

The concentrations of elemental carbon and its fluxes were determined in Lake Whitney sediments (Table I). The maximum flux occurred in the mid- to late 1950's and had decreased by 1964, perhaps resulting from better emissions control. A sample from 26-27 cm was compared morphologically (SEM) to carbon particles produced by the burning of coal, oil, and automobile exhausts (Figure 8). By comparing with pictures in the Particle Index, the preponderance of carbon particles isolated from Lake Whitney sediments resembled particles produced from coal, wood, and oil burning. Automobile exhaust carbon may also be present but is difficult to distinguish from the other carbon particles. Coal- and wood-derived particles are differentiated from other carbon particles by significant contents of Si, Fe, Al, and Cu (as determined by EDAX). The other carbon particles had no peaks on the EDAX, probably due to loss to the acid and base leaches during isolation of the carbon particles. The presence of carbon particles derived from coal and oil usage clearly indicates that metals associated with their fly ash are reaching Lake Whitney sediments. Sources of coal and oil burning other than United Illuminating, perhaps factories and homes in close proximity to the lake, predominate.

Lead. Anthropogenic fluxes for lead in the Lake Whitney core are first evident in the mid-1800's and reach a maximum

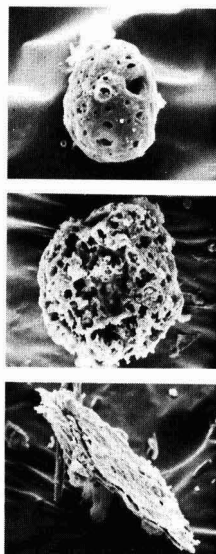


Figure 8. SEM photographs of elemental carbon particles chemically isolated from Lake Whitney sediments. Bottom particle believed to have originated from wood burning due to its morphology and Si and Al contents. Upper two probably originated from coal and/or oil burning.

of 650 $\mu\text{g}/\text{cm}^2/\text{yr}$ in 1965, then drop sharply to 195 $\mu\text{g}/\text{cm}^2/\text{yr}$ for 1975.

The sources of Pb in the sediments may be obtained by studying the lead isotopic ratios. Chow et al. (6) have shown that the lead aerosols produced through coal burning and automobile exhausts carry identifying isotope ratios. These ratios originated in the deposits from which the leads were mined.

If the amounts of lead aerosols are high enough, they can change the isotopic ratios in the soils. In the sediments of Lake Whitney, the lead ratios listed in Table III appear to be constant for samples below 48 cm (1858) and reflect radiogenic leads in the glacial till. Above 48 cm they begin decreasing until 18–19 cm (1956), at which time they increase slightly to the present. Comparing the lake sediment isotopic ratios with those for the alkyl additives in gasoline from Boston, Mass., in 1964 and for coal indicates that coal consumption and the general industrial growth of New Haven were the main sources of lead in the late 1800's and early 1900's and were replaced by gasoline lead as the primary source after the 1920's.

Lake Whitney has several well-traveled roads in its drainage area. One of these roads, Whitney Avenue (formerly the Hartford Turnpike), closely parallels the lake at distances often less than 5 m. It crosses the northern end of the lake and then runs along the west side of Lake Whitney. Storm and runoff drainage from Whitney Avenue is routed into Lake Whitney. Up to 1966, Whitney Avenue was the major northerly route from the suburbs to New Haven and was heavily traveled. In 1966 a new turnpike, Interstate 91, was opened paralleling Whitney Avenue but sufficiently to the east to be out of the Lake Whitney drainage area.

A sudden decrease in traffic volume along Whitney Avenue resulted. This would decrease the amount of lead reaching the lake through the air and in the storm drains. Work by Habibi (13, 14) has shown that over one-half of the lead emitted through automotive exhaust systems falls out within 7 m of the source. The remainder, less than 9 μ in diameter, is deposited farther away depending upon the wind conditions and obstructions. Thus, when I-91 opened and the traffic volume on Whitney Avenue decreased, the amount of Pb entering the lake also decreased.

The sediments where the core was taken in Lake Saltonstall do not receive any near fallout of Pb from major highways. Therefore, its sediments reflect only the long-range transport

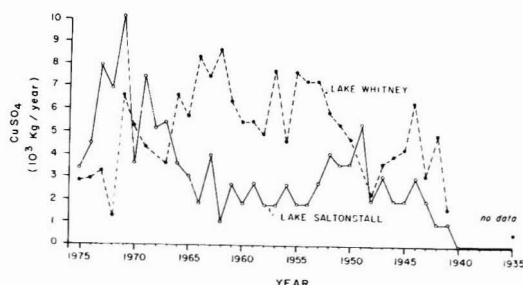


Figure 9. CuSO_4 additions to Lake Whitney and Lake Saltonstall since 1935

of Pb from the ever-increasing volume of automobile traffic in the New Haven area.

Copper. Many reservoirs add a biocide, primarily CuSO_4 , to limit the population of bacteria, diatoms, and algae. The amounts to be added are determined by the degree to which their water intake filters become clogged with organisms.

Both Lake Whitney and Saltonstall have had higher fluxes of organic matter and skeletal remains to their sediments in the last 20 years (Table I), although Lake Whitney shows a recent decrease in opal content. CuSO_4 additions to the reservoirs (Figure 9) seem to reflect the biological productivity as recorded in the sediments (Table I). When comparing Figure 9 with Figures 6 and 7, the pattern of Cu concentrations in Lake Whitney and Saltonstall closely parallels the CuSO_4 additions. The very high copper concentrations in the sediments of both lakes result from the addition of CuSO_4 by the New Haven Water Co.

The flux of anthropogenic Cu in the sediments can be compared to the CuSO_4 flux if one assumes that the CuSO_4 was equally distributed over the whole lake (Table II). The sedimentary Cu flux is about two times greater than the CuSO_4 flux. However, since more CuSO_4 was added nearer the dams, the agreement is not unreasonable.

Other Sources. The increases in metal concentrations in the more recent Lake Saltonstall sediments (Figure 4) follow roughly the pattern of population growth in the East Haven area (2) (Figure 1). Perhaps the source of the metals is not unique, but disperse origins such as backyard sewage disposal, burning of home heating oils, and general industrial activity account for the observed concentrations.

The metal concentration patterns with time in Lake Whitney sediments are more difficult to interpret since many of them show maxima in the past. Such patterns are more suggestive of a single source of any specific element since the population in Hamden (north New Haven) has increased in recent times. The different times of the maximum concentration for the various elements indicate more than one source was probably operating over the time interval considered. Possible sources include electrical power generating stations for the railroad lines, one of which parallels the Mill River for many miles, industrial discharge and fossil fuel burning, burning of home heating oil, or sewage discharged into the drainage area.

Acknowledgment

T. J. Chow determined the lead isotopic ratios, and K. Gaugler the elemental carbon concentrations. We are most grateful to the New Haven Water Co. and the staff of Yale University. Without their assistance this project could not have been finished. We thank E. D. Goldberg and his colleagues at Scripps Institute of Oceanography for their cooperation, assistance, and review of this manuscript.

Table III. Lead Isotope Ratios in Lake Whitney Sediments

Depth (cm)	Year	Pb_{206}^{206}	Pb_{207}^{206}	Pb_{208}^{206}	Pb concn ($\mu\text{g}/\text{g}$)
1–2	1974	18.91	1.2021	0.4901	707
10–11	1965	18.77	1.191	0.4869	1100
18–19	1956	18.64	1.179	0.4826	470
26–27	1948	18.78	1.190	0.4822	270
34–35	1912	18.93	1.202	0.4880	170
38–39	1896	19.22	1.216	0.4880	170
43–44	1877	19.77	1.241	0.4926	100
48–49	1858	20.79	1.302	0.5103	100
53–54	1839	20.90	1.305	0.5076	44
56–57	1827	20.50	1.291	0.5057	40
Gasoline ^a					
Boston, Mass.	1964	18.45	1.179	0.4819	...
Coal ^a					
Ashley, Pa.	...	18.64	1.189	0.4824	34
Jeddo, Pa.	...	18.82	1.197	0.4850	11
Trevorton, Pa.	...	18.82	1.200	0.4849	10
St. Nicholas, Pa.	...	18.79	1.199	0.4849	14

^aRef. 6.

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Color Removal from Softwood Kraft Pulp Bleach Plant Effluent by Polyamines

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Color bodies from a freeze-dried, softwood kraft caustic extract effluent and from a partially purified, acid-precipitated color body fraction (Fraction I) precipitated when treated with polyamines. Against caustic extract effluent color, each polyamine had a pH range yielding optimal color removal. The largest polymer studied, PEI 18 (a branched polymer of ethyleneimine M_n 1800 \pm 300), was the most effective precipitant, achieving 85-90% color removal at pH to 8.5 and polyamine concentrations of 550-800 ppm. Lower molecular weight polyamines (tetraethylenepentamine to ethylenediamine) were less effective. Fraction I color bodies were far more easily precipitated. Color removal and precipitate composition were dependent upon both the cationic character of the polyamine and the anionic character of the color bodies. The precipitate retained the ionic character of the reacting species and contained only small amounts of inorganic counterions. Conductivity and zeta potential measurements were used to probe the mechanism of precipitation from Fraction I, and a general mechanism was proposed, involving a rapid initial interaction based on coulombic attraction, which ultimately leads to the formation of larger aggregates that precipitate.

In recent years the pulp and paper industry has markedly improved the quality of effluents discharged to the aqueous environment. However, one of the most difficult environmental problems, that of removing effluent color, remains to be adequately solved. In bleached kraft mills, 60-70% of the total color is typically derived from one effluent stream, the first caustic extract after chlorination (1, 2). A variety of methods for removing color from caustic extract effluents have been fairly effective in some situations. These include precipitation by di- and trivalent metal cations (3, 4), ion ex-

change (5), adsorption by activated charcoal (6) or synthetic resins (7), reverse osmosis (8), chemical (9) or photochemical oxidation (10), and phase separation using long chain aliphatic amines, emulsified in hydrocarbon solvents (11).

This work presents a new method for removing soluble color: the precipitation of color bodies by polyamines. The polyamines studied were PEI 18, 12, and 6 (branched polymers of ethyleneimine, M_n 1800 \pm 300, 1200 \pm 200, and 600 \pm 100, respectively), tetraethylenepentamine, triethylenetetramine, diethylenetriamine, ethylenediamine and its symmetrical *N*-methyl-substituted analogs (di- through hexamethyl), 1,3-diaminopropane, 1,4-diaminobutane, 1,12-diaminododecane, and ethylamine.

Results

Table I shows the color removals obtained from several caustic extract effluents when treated with PEI 18 at pH 7. In this work, all color measurements were made by determining the optical density at 450 nm. APHA color units were not determined, but the values in parentheses in Table I were estimated by multiplying by 4400. Color removal levels were determined by measuring the optical density after treatment and then determining the optical density of the effluent at the same pH. In most work, color is always determined at a specific pH (e.g., 7.6), but this was not practical in the present work since such pH adjustment could lead to further precipitation. Color removal levels of 89-96% were obtained with all the effluents tested, although some variation in the PEI 18 requirement was noted. Precipitation was rapid, and the dense precipitate formed appeared to have good settling properties. To gain further insight into the factors that are important in precipitation, Mill A effluent was selected for study and freeze-dried for use as a caustic extract standard (CES).

Color Removal from CES. Color removal from CES by

Table I. Color Removal from Caustic Extract Effluents by PEI 18 at pH 7

Mill	Fiber source	Initial color OD (ϵ , 450 nm (color units) ^a	Max color removal, %	PEI concn required, ppm
A	Mixed softwood	3.2 (14 000)	89	600
B	Mixed softwood	4.0 (18 000)	96	400
C	Ca. 95% softwood, 5% hardwood	4.6 (20 000)	95	800
D	70% softwood, 30% hardwood	3.1 (14 000)	92	200

^a Estimated by multiplying optical density by 4400 (National Council of the Paper Industry for Air and Stream Improvement, Tech. Bull. 253, Dec. 30, 1971).

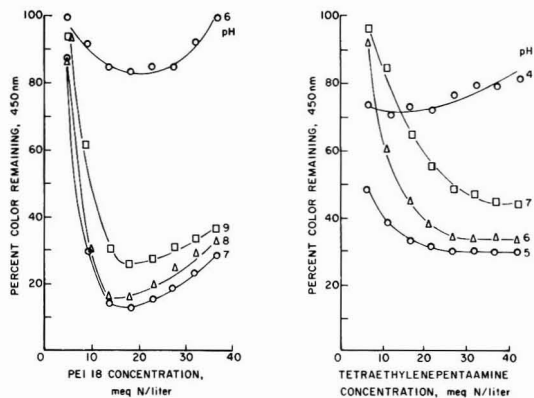


Figure 1. Color removal from CES by PEI 18 and tetraethylenepentamine

PEI 18 at several pH's is shown in Figure 1. This polyamine was the most effective precipitant, achieving 85–90% color removal at the optimum pH range of 7–8.5, at PEI 18 concentrations of 12–18 milliequivalents of nitrogen per liter (meq N/L) i.e., 550–800 ppm. Under these conditions, the addition of PEI 18 caused an instantaneous turbidity, followed by the formation of a dense precipitate that settled rapidly. Color removal was dependent upon both the pH of the precipitation medium and the polyamine concentration. When the PEI 18 was in excess of that required to achieve maximum color reduction, the percent color removal observed decreased. These nonoptimal conditions produced a suspended precipitate, which settled only slowly. Color removal by PEI 12 and 6 showed a trend toward higher pH optima, higher optimum polyamine concentrations, and lower color removal.

The low molecular weight linear polyamines also removed CES color, but less effectively than PEI 18. As before, color removal showed an optimum pH range (Table II), but the optima occurred at acidic conditions and decreased with decreasing molecular weight, as did the ultimate color removal levels observed (Table II). The presence of excess polyamine had little effect on maximum color removal, as shown in Figure 1 for tetraethylenepentamine. However the *rate* of precipitation increased with increasing polyamine concentration.

Of the diamines tested, only ethylenediamine and 1,12-diaminododecane removed color. Ethylenediamine was weakly effective, removing about 20% of CES color at concentrations of 40 meq N/L or more at pH's 4 and below. In contrast, 1,12-diaminododecane was able to achieve 70% color removal at concentrations of about 30 meq N/L at pH's 8 and below. Diamines of 3 and 4 carbons, and *N*-methyl analogs of ethylenediamine gave essentially no color removal. The greater color removal observed for 1,12-diaminododecane was

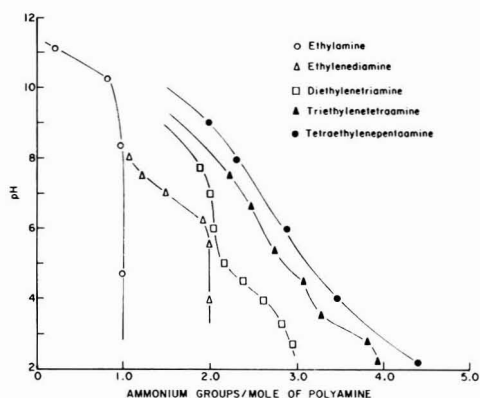


Figure 2. Polyamine protonation as a function of pH

attributed, at least in part, to differences in polyamine–solvent (water) interactions resulting from the presence of the 12 carbon chain, and no attempt was made to correlate its effects with those of the other polyamines.

Polyamine Protonation at Optimum pH. The degree of protonation at optimum pH was determined by titration for several of the polyamines of interest (Table II). Titration curves are shown in Figures 2 and 3. These figures show that as the number of amino groups per molecule increases, the individual pK_a 's become blurred. For di- and triamines the pH optima corresponded to completely or nearly completely protonated species. Triethylenetetraamine produced maximum color removal at 75% protonation, i.e., three cationic sites per molecule. With tetraethylenepentamine, maximum color removal occurred at 60% protonation, which also corresponds to three cationic sites per molecule. The pH optima for the PEI series occurred at percent protonations of 35–50%. Thus, the trend established is that dications can remove CES color, but triprotonated species are more effective. When the number of potential cationic sites exceeds three, color removal is favored by increasing charge separation (i.e., larger molecule) until an apparent optimum separation is reached (PEI series).

While these data indicated that the cationic character of the polyamine was important in the precipitation, very little could be inferred about the role of the color bodies. To obtain a clearer view of the role of color bodies in precipitation, color removal was also studied using a partially purified, more readily precipitated color body fraction obtained from CES by acid precipitation. This material (Fraction I) represented 40% of the original CES color and about 10% of the initial solids. Fraction I color bodies had higher molecular weights and were less acidic than the average CES color bodies.

Color Removal from Fraction I. Fraction I color bodies

Table II. Polyamine Protonation at Optimum Color Removal

Polyamine	Max color removed, %	Optimum pH	Protonated sites per molecule	
			At optimum pH	%
Ethylenediamine	20	4–3	2.0	100
1,12-Diaminododecane	70	8–7	2.0	100
Diethylenetriamine	50	4–3	2.6–2.9	86–97
Triethylenetetraamine	70	5–4	2.7–3.3	66–83
Tetraethylenepentamine	70	6–5	2.9–3.2	58–64
PEI 6	75	9.0–8.5	4.6–6.1	33–44
PEI 12	85	8.5–7.5	10.5–14.7	35–49
PEI 18	89	8.5–7.0	13.8–20.5	33–50

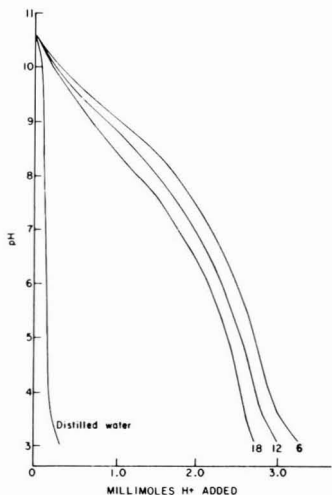


Figure 3. Titration of PEI 18, 12, and 6 with hydrochloric acid (at 3.7 meq N/200 mL, in 2000 ppm sodium chloride)

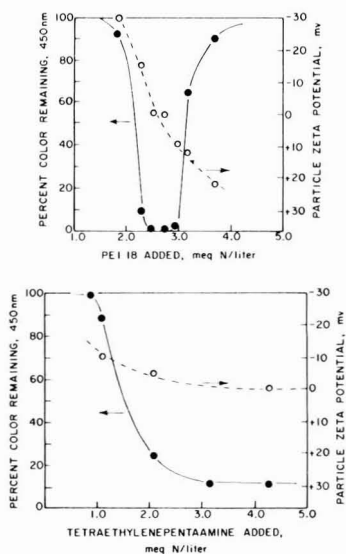


Figure 4. Zeta potentials of Fraction I particles precipitated at pH 7

were far more easily precipitated than those of CES. When PEI 18 was tested, color reductions of 95% or more were observed at pH's between 4 and 9. Both PEI 12 and 6 showed similar levels of color removal. The effect of decreasing pH was to decrease the solution concentrations of the polyamines required to achieve these levels. The effect of excess polyamine varied. With PEI 18 at pH's 4-9, or PEI 12 at pH's 8 and below, excess polyamine decreased color removal sharply, as shown in Figure 4 for pH 7. With PEI 6, or PEI 12 at pH 9, the color removal profiles were relatively unaffected by excess polyamine, showing that the shape of the color removal curve was dependent upon the number of cationic sites per molecule. When tetraethylenepentamine was the precipitant, almost 90% color removal was observed at pH 7 (Figure 4) and below. Excess polyamine had no effect on the ultimate color removal level. In contrast, color removal by diethylenetriamine was

strongly dependent upon the pH of the precipitation medium. At pH 7, where the triamine was doubly protonated, only 50% color removal was produced at concentrations of 30 meq N/L or more. As the pH decreased, increasing the cationic character of the triamine, color removal increased; at pH 4, 3 meq N/L gave about 91% color removal.

Precipitate Polyamine Content. The polyamine contents of several CES and Fraction I precipitates were determined directly by total nitrogen analysis of the precipitates, and by difference, using a spectrophotometric method for determining supernate polyamine concentration. When both methods were applied to the same samples, the results were in agreement. When the compositions of CES and Fraction I precipitates were normalized for color removal and compared, color removal by the linear polyamines was roughly proportional to both precipitate dry weight and polyamine content. When the normalized PEI 18 precipitate compositions were compared, the PEI 18-CES precipitate contained far more PEI 18 per unit of color removed than from Fraction I. Therefore, color removal from CES involved the precipitation of at least two types of materials: color bodies typified by Fraction I, which could be precipitated by all of the polyamines, and those species (colored and/or colorless) soluble at pH 1, which were precipitated only by the larger branched PEI's.

When the polyamine contents of various Fraction I precipitates were compared on the common basis of milliequivalents of *ammonium ion*, obtained by multiplying precipitate amine content by the fraction of amino groups protonated (determined by titration), the values were approximately constant at each pH (Table III). The amount of polyamine in the precipitate appeared to be directly proportional to the cationic character of the polyamine in solution.

The anionic character of the color bodies was also a function of pH. Figure 5 shows titration curves for CES and Fraction I, the latter being at 1/10th the concentration of the former, since it represented 10% of the material in CES. The largest fraction of the acidic groups had pK_a 's of less than six. Table III also shows that as the pH of the precipitation medium increased, the polyamine ammonium ion equivalents increased. Since the anionic character of the color body fraction in solution increased with increasing pH (Table III), it is reasonable to conclude that the polyamine content of the precipitate was also dependent upon the anionic character of color bodies. As can be seen, the increase in the number of anionic sites in Fraction I paralleled the increase in precipitate ammonium ion equivalents.

Ionic Character of Precipitate. Infrared spectroscopy of the dry precipitates from CES and Fraction I precipitated with diethylenetriamine showed that the carboxyl/carboxylate ratio of the color bodies was essentially the same before and after precipitation by polyamines. Hence, the precipitate retained the ionic character of the color bodies and presumably of the polyamines; proton transfer from a cationic group to carboxylate anion to yield two uncharged species was not extensive, if indeed it occurred at all.

Phenolate and enolate protonation is more difficult to eliminate. Although caustic extract contained very little phenols, both were implicated in color body precipitation with lime (12). The infrared spectra did not show differences that could be attributed to such protonation, and the optimum pH range for some polyamines appeared to be out of the range of pK_a 's for such functional groups.

Analysis of precipitate inorganic counterion content showed that the total sodium and chloride content was less than 7% of the ionic equivalents attributed to the color bodies and polyamines, showing that both localized and overall electrical neutrality was achieved primarily through the association of color body anionic sites with polyamine cationic sites.

Table III. Polyamine Content of Various Fraction I Precipitates^a

	Protonatable groups ^b in Fraction I (meq/L)	Meq of ammonium groups ^c in precipitates from			
		PEI 18	Tetraethylenepentamine	Diethylenetriamine	1,12-Diaminododecane
pH 7	1.31	1.11	0.99	0.96	0.92
pH 6	1.08	0.90	0.88
pH 5	0.89	0.73	0.77	0.63	...
pH 4	0.58	0.67	0.61	0.62	0.66

^a Normalized to 100% color removal from 1 L of Fraction I. ^b Obtained by titration from given pH to pH 2. ^c (meq N/L) (% protonation)/(% color removed).

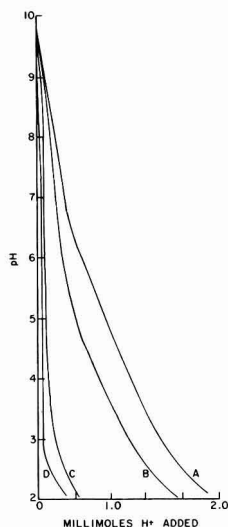


Figure 5. Titration of CES and Fraction I with hydrochloric acid [A: CES 0.91 g/50 mL; B: A after acidification and vacuum degassing with pH adjustment; C: Fraction I 0.091 g/50 mL; D: distilled water (50 mL) plus sodium hydroxide to pH 9.5]

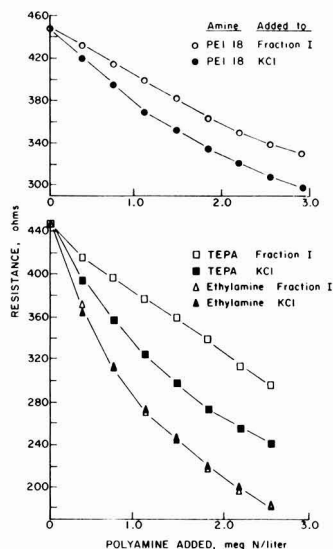


Figure 6. Resistivity as a function of polyamine addition to pH 7 solutions of Fraction I and potassium chloride

Conductivity and Zeta Potential Measurements. The early stages of precipitation of Fraction I color bodies were examined by comparing the changes in conductivity as polyamines were added to Fraction I with the changes as polyamines were added to a KCl control solution having the same initial pH and conductivity as Fraction I. The results are shown in Figure 6. The addition of either PEI 18 or tetraethylenepentamine decreased the resistance of Fraction I solutions, but the decrease was significantly less than observed when these amines were added to the KCl solution. When ethylamine was added, the decrease in resistance was the same for both solutions. From these results, it was concluded that the polyamines complexed with Fraction I components, decreasing the number and/or effectiveness of the charge carrying species. Complexation was rapid and could occur even at nonprecipitating polyamine concentrations.

The later stages of precipitation of Fraction I color bodies were examined by determining the zeta potential of precipitated particles. When either PEI 18 or tetraethylenepentamine was the precipitant, the particles formed on the initial portion of the color remaining curve showed negative zeta potentials (Figure 4). As the PEI 18 concentration was increased, the zeta potentials became less negative and passed through zero at maximum color removal. On the ascending portion of the color remaining curve, where PEI 18 was present in excess, positive zeta potentials were observed. In contrast, as tetraethylenepentamine concentration was increased be-

yond the point of increasing color removal, the zeta potentials of the particles remained slightly negative to zero, even in the presence of excess polyamine. When the order of addition was reversed, i.e., when color bodies were added to polyamine, the zeta potential of the precipitate showed the same behavior. Thus, it was not possible to build up a positive surface charge when tetraethylenepentamine was the precipitant.

Discussion

Mechanism of Precipitation of Fraction I Color Bodies.

The results obtained show that color removal involves interactions between the anionic color bodies and the cationic polyamines and are consistent with the following general mechanism. At a given pH there are a number of anionic color body sites. As polyamine at the reference pH is added, a coulombic interaction leads to complex formation. The formation of the complex is rapid and occurs even at nonprecipitating polyamine concentrations. The complexation results in a decrease in the net negative charge on the color bodies. As more polyamine is added, the size of the complex increases, and aggregates form. The addition of more polyamine promotes further aggregation, either by intimate association with a portion of the remaining anionic sites, or by depressing the electrical double layer in accord with the Derjaguin-Landau, Verwey-Overbeek (DLVO) theory of colloidal stability (13), thus enhancing the likelihood of aggregate association and subsequent precipitation. The pre-

cipitate retains the ionic character of the interacting species, and both overall and localized electrical neutralities are achieved primarily by the association of anionic color body sites with cationic polyamine sites.

As the number of cationic sites per polyamine molecule increases, color removal increases and the solution concentration required to achieve maximum color removal decreases. The enhanced color removal must be attributed to the increasing cationic character of the polyamine. When the polyethyleneimines were the precipitants, color removal was more rapid than with the low molecular weight polyamines. These branched polyamines are larger and contain many more cationic sites per molecule. This would lead to larger initial complexes and aggregates. The decrease in color removal when PEI 18 was present in excess can be attributed to the reversal of charge on the particles due to the binding of more than the stoichiometric amount of the cationic polyamine. That no positively charged species were detected when tetraethylenepentamine was the precipitant shows that linear polyamines cannot be complexed in sufficient quantity to bring about charge reversal.

To determine whether color removal from Fraction I could be explained as a solubility product (K_{sp}) phenomenon, the effects of dilution on color removal by tetraethylenepentamine were determined. The concentration of tetraethylenepentamine required to either initiate or achieve maximum precipitation decreased with Fraction I dilution. This observation suggests that color removal cannot be explained as a classical K_{sp} phenomenon.

Mechanism of Color Removal from CES. There is evidence to suggest that the Fraction I mechanism can be extended to account for color removal from CES.

- The relative order of effectiveness and qualitative rates of precipitation for the various polyamines were similar in both color body systems.
- Both systems showed similar color removal profiles and enhanced precipitation when tricationic species were present.
- The diethylenetriamine, pH 4 precipitates from CES and Fraction I showed similar nitrogen contents, and color removal was proportional to precipitate dry weight. The same is true for tetraethylenepentamine at pH 5 with both color body systems.

Since both systems showed similar behavior, similar mechanisms are probably operative. However, some differences were also noted:

- The polyamine content of Fraction I-PEI 18 precipitates was much lower than that found in the CES-PEI 18 precipitates. These differences are reflected in the lack of proportionality between color removal and precipitate dry weights.
- With CES the polyamines showed definite pH optima, whereas this was not observed with Fraction I.

Presumably, a portion of these differences can be attributed to interactions with the soluble supernate components which were not present in the acid-precipitated material (Fraction I).

Experimental

CES was prepared by freeze-drying Mill A caustic extract after pressure filtration through a 0.45- μ m Millipore filter. Freeze-drying has little effect on caustic extract color or sedimentation coefficient, even with long periods of storage (14). In reconstitution a measured amount of CES was dis-

solved in distilled water. After 15–20 min of stirring, the pH of the sample was adjusted as desired, and the sample was diluted to twice the original CES concentration, or 0.910 g/50 mL.

To determine color removal, an aliquot of this 2X CES solution was transferred to a sample tube containing a known amount of water, the solutions were mixed, and the desired amount of polyamine at the desired pH was added with mixing. The pH was readjusted if required. In all cases the final volume was such that CES was at its original concentration (0.910 g/100 mL). The solutions were capped and stored in the dark at 20 °C for 24 \pm 1 h. Then the samples were centrifuged, and the absorbance of the supernate at 450 nm was determined. A control sample was prepared at the same pH, but without polyamine. Data were expressed as percent of the original 450-nm absorbance remaining. Precipitates were washed with distilled water, freeze-dried, and weights recorded.

Fraction I was obtained by acidifying a concentrated (9X) solution of CES to pH 1 with concentrated HCl. After 18 h at 4 °C, the precipitate was collected by centrifugation, resuspended in distilled water, and freeze-dried. Reconstitution was as for CES except that NaOH was added to give pH 7–8 during the initial resolubilization. Color removal was determined as described above.

The total nitrogen content of precipitates was determined using a Coleman nitrogen analyzer. Supernate polyamine concentrations were determined using the method of Kindler (15), except that the optical density at 290 nm was followed, and the samples were made 0.04 M in lead acetate, pH 5.3, to prevent complexation of the color bodies with the cupric ion.

Zeta potentials were determined using a Model B, Zetameter, (Zetameter Inc., New York, N.Y.).

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New Heterogeneous Mode of Nitric Oxide Reduction by an in Situ Formed Carbon

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■ A highly reactive, carbonaceous reductant for NO is found on portions of heated reactor walls exposed to HC (hydrocarbon) + O₂ mixtures richer than optimum for homogeneous reduction of NO. This reductant reduces as much as 95% of the NO for prolonged periods. The duration of the reduction process is a function of the duration of deposition, temperature, residence time, and [O₂]/[HC] ratio, whereas the extent of NO-reduction is a function of the temperature, [O₂]/[HC] ratio, and residence time. In addition, an activation energy of 34 kcal is indicated. Residence times are compatible with those of automobile exhaust, and comparisons are made with previous observations of the SCR Mode in engine tests. The isolation, characterization, and products of the SC reductant are described.

In the course of a study on the chemistry of the homogeneous reduction of nitric oxide in simulated exhaust effluents by hydrocarbon (HC) oxygen mixtures (1), a new and unique heterogeneous mode of efficient NO reduction was observed. The homogeneous gas-phase reduction had been accomplished previously by injecting various mixtures of HC and O₂ into a high-temperature stream (1200–1700 K) of simulated combustion effluent containing NO, CO, and CO₂ in N₂, flowing through a tubular, ceramic reactor. The new mode of reduction manifests itself as a failure of the NO concentration to return to its original, unreduced level after termination of the reducing flow of HC plus O₂. The NO then drops to an even lower level, which can be as low as a few percent of the original NO concentration, and has been observed to remain at the lowest level for as long as 5 h.

This phenomenon, observed from approximately 1300 to 1700 K, has been interpreted in terms of the formation of a carbonaceous NO reductant on the wall of the reactor tube during the course of the homogeneous reaction. The heterogeneous reaction becomes dominant only when injection of the gas-phase reductant is discontinued. This new mode of reduction, called the self-contained reductant mode (SCRM), was investigated on the basis of this hypothesis. While the reaction of NO with carbon has been well studied, this in situ phenomenon involving nitric oxide, oxygen, and hydrocarbon is unique in that it presents a group of new parameters and relationships that function under combustion effluent conditions. As far as practicality is concerned, it is not the intention of this paper, nor is it possible at this time to prove applicabilities to IC engine or other exhaust. On the other hand, there appears to be enough latitude for creative modification of the principle, so that one cannot outright reject possibilities for the future. In this respect, one must remember that the observed residence times are compatible with a reactor functioning in a stream of automobile exhaust.

The investigation of this reduction process falls into two categories: the reduction criteria as a function of the numerous parameters that control them, and the chemical and physical nature of the isolated SC reductant itself, including a quantitative and balanced analysis of the reactants and products.

Since this is a study of the heterogeneous reaction of a form of carbon with nitric oxide, the literature so pertaining might seem to be the most relevant. However, the emphasis of this paper is on the parameters involved in forming and then oxidizing with NO, the SC reductant under these unique conditions. No previous publications on this subject have been noted.

The literature on the carbon-NO reaction is fairly detailed, but among the latest investigations are those of Edwards (2) and Tucker (3), which provide an extensive literature review. Although application to pollution control was considered, these works are principally flow reactor studies of the reaction of NO with graphite and activated carbon, respectively. Edwards concluded that even graphite resistant to oxygen could effect appreciable reduction of NO at 1233 K, with an activation energy of the order of 21 kcal mol⁻¹. Tucker measured the reaction of NO with activated carbon with a number of different additives, including O₂ (which enhanced the rate considerably), H₂, CO, and CO₂, up to temperatures of 1111 K. He found an activation energy of 32 kcal mol⁻¹. For a detailed review, the reader is referred to ref. 3.

In the present study the principal reduction criteria are fractional reduction in NO concentration, [NO]_f/[NO]_i (final over initial NO concentration), caused by the SCR mode and the duration in seconds, τ_R, for which this reduction mode is maintained. The important controlling parameters are the conditioning or reacting temperature, T; the duration of the conditioning process or conditioning time, τ_c; the residence time of an element of the gas in the reactor, τ_{res}, and the [O₂]/[HC] ratio (moles of oxygen to moles of hydrocarbon) of the conditioning gas flow. The term "conditioning" refers herein to the process by which the SC reductant is formed on the reactor walls.

Finally, a description is given of the isolated carbonaceous reductant in terms of both chemical and electron microscopic analysis, and of a balanced chemical analysis of the reactant and product gases.

Experimental

The ceramic flow reactor and related apparatus used here are the same as described in the previous paper (1) on the gas-phase reaction, except that all experiments were carried out with the larger 3/4-in i.d., mullite tube. Connections to the flow reactor were improved both with respect to leakage and convenience of removal by replacing the Sauereisen cement connections with high-temperature stainless steel flanges. Temperatures were measured with the same considerations previously discussed, using Pt-Rh thermocouples cemented onto the *outside* of the reactor tube. These thermocouples had been first calibrated by means of thermocouples on the *inside* of the tube, as a function of all flow and temperature parameters involved. The special technique used to isolate and locate the SC reductant will be considered along with the results of that phase of the research in the latter part of this paper.

Results and Discussion

The SCR mode was first observed during gas-phase NO-reduction experiments using simulated auto exhaust effluents in which the [O₂]/[HC] ratio, R₃, was richer than optimum (1), i.e. [O₂]/[C₁] = 0.75 to 1, or for the case of isobutane, R₃ = [O₂]/[i-C₄H₁₀] = 3 to 4. Stoichiometric for the combustion of isobutane to CO₂ is 6.5, so that the optimum R₃ is usually 1/2

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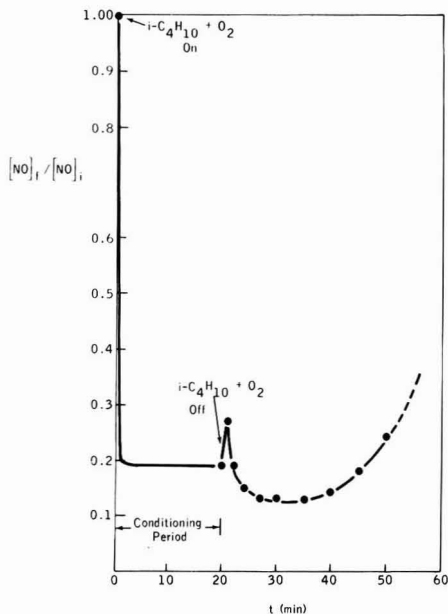


Figure 1. Nitric oxide concentration as a function of time for typical SCR mode reduction

$T = 1509 \text{ K}$; $\tau_{\text{res}} = 190 \text{ ms}$; $[i\text{-C}_4\text{H}_{10}] = [\text{O}_2] = 0.4\%$ and $[\text{NO}]_i \approx 1000 \text{ ppm}$ in N_2

of the stoichiometric value. When a gas-phase reduction is carried out with a richer-than-optimum $R_3 = [\text{O}_2]/[i\text{-C}_4\text{H}_{10}] = 1$, where $[\text{O}_2] = 0.4\%$, $[\text{NO}]_i = 1000 \text{ ppm}$, and $T = 1059 \text{ K}$, the phenomenon described in Figure 1 is observed. After a steady-state homogeneous reduction of $[\text{NO}]$ to less than 200 ppm has been maintained for 20 min, the reducing flow is cut off. The value of $[\text{NO}]$ first rises some 100 ppm before dropping down again, so that within 5 min of cut-off, $[\text{NO}]$ is considerably lower than 200 ppm ($\sim 125 \text{ ppm}$). This low level of NO is maintained for approximately 20 min before the NO concentration begins to increase slowly toward the initial concentration, $[\text{NO}]_i$.

An example of extended reduction by this mode, under extreme conditions, where $T = 1673 \text{ K}$ and $R_3 = 0.54$, is given in Figure 2. Here 10 min of conditioning provide essentially 100% reduction of the 1000 ppm NO for over 3 h. This represents an efficiency, based on the theoretical reduction of one NO per C-atom from $i\text{-C}_4\text{H}_{10}$, of roughly 83%, which is quite high compared to results at lower temperatures. Note that in neither case was CO_2 or CO present in the gas mixture.

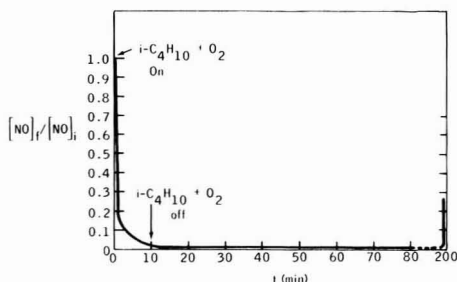


Figure 2. Long duration nitric oxide reduction by SCR mode

$T = 1673 \text{ K}$; $\tau_{\text{res}} = 100 \text{ ms}$; $[i\text{-C}_4\text{H}_{10}] = 0.65\%$; $[\text{O}_2] = 0.35\%$ and $[\text{NO}]_i \approx 1000 \text{ ppm}$ in N_2

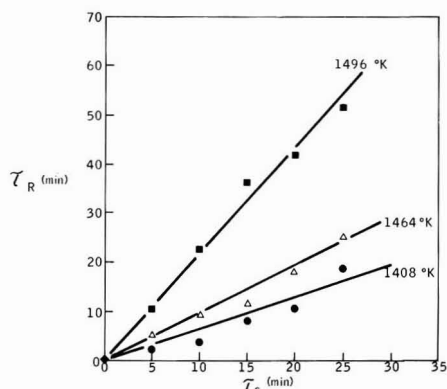


Figure 3. Duration of nitric oxide reduction (τ_R) as a function of conditioning time (τ_c)
 $\tau_{\text{res}} = 180\text{--}192 \text{ ms}$; $[i\text{-C}_4\text{H}_{10}] = [\text{O}_2] = 0.4\%$, and $[\text{NO}]_i \approx 1000 \text{ ppm}$ in N_2

The first phase of the results places on a quantitative basis the effectiveness of the SCR reductant (in terms of $[\text{NO}]_t/[\text{NO}]_i$ and τ_R) as a function of T , R_3 , τ_{res} , and τ_c . The effective survival time (in minutes) of the SCR reductant, τ_R , is taken as the interval of time which starts when $[\text{NO}]$ drops below an increment of 100 ppm above the SCR $[\text{NO}]$ minimum to the time when it rises above the 100 ppm difference. The residence time, τ_{res} (ms), in the reactor is taken as the time spent by a reacting gas element in the hottest, central, 12 in. of the heating core of the furnace. The temperature gradient was greatest down- and upstream of this core.

Conditioning and Preconditioning Prerequisite. No SCR phenomenon whatsoever is exhibited by the fresh wall of a new, ceramic reactor tube. It is necessary to recycle some 3–6 times, the normal SCR conditioning procedure (20-min exposures to the $\text{HC} + \text{O}_2 + \text{NO}$ mixture) before the SCR manifests itself in a new tube. Once the tube is preconditioned, the SCR proceeds in a reproducible manner. The data of the experiments described herein yield smooth, monotonic curves typical of the many results obtained. By maintaining very clean walls and high purity in the gas mixtures, good reproducibility was forthcoming, so that confidence limits of about $\pm 15\%$ were readily established for the final curves, and the mean deviation for the points of most curves was under that. While no research was undertaken toward the elucidation of the preconditioning, it seems likely that active sites on the high specific area ceramic (mullite: $2\text{SiO}_2\text{-Al}_2\text{O}_3$) must be saturated with reductant-forming free radicals before active SCR reductant can begin to form.

Duration of SCR Mode. If the basic process here is one of synthesizing a reductant on the reactor walls from $\text{HC} + \text{O}_2$, then one would expect a correlation between the length of time, τ_R , during which the reductant remains active and a number of independent variables. The variables for which quantitative relationships have been found and are herewith described are τ_c , the conditioning time; T , the absolute temperature; τ_{res} , the residence time; and R_3 , the $[\text{O}_2]/[\text{HC}]$ ratio.

Effect of Conditioning Time and Temperature. τ_R is essentially a linear function of τ_c at constant temperature. This is shown in Figure 3 and represents conditioning with a mixture of 0.4% each of $i\text{-C}_4\text{H}_{10}$ and O_2 , along with 0.1% NO in N_2 where $\tau_{\text{res}} = 188 \text{ ms}$. The linearity corresponds to a process that synthesizes and then consumes the reductant at a constant rate.

From these $\tau_R - \tau_c$ relationships, curves showing the effect of temperature on τ_R at constant τ_c have been plotted as

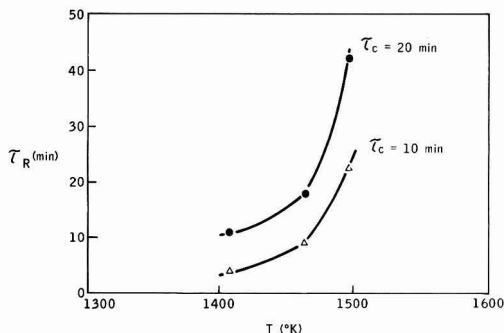


Figure 4. Duration of nitric oxide reduction (τ_R) as a function of temperature

$\tau_{res} = 188\text{--}192$ ms; $[i\text{-C}_4\text{H}_{10}] = [\text{O}_2] = 0.4\%$, and $[\text{NO}] \approx 1000$ ppm in N_2

shown in Figure 4. The rapidly rising values of τ_R imply the usual chemical kinetic exponential temperature dependence. This must be descriptive of the deposition process that provides the NO reductant. If the exponential dependence is present in the reduction process, it obviously would have to possess a much weaker temperature function since, as we shall see later, the fractional reduction in NO increases or improves with increasing temperature.

The dependence of τ_R can be summed up by a speculative expression:

$$\tau_R \propto \frac{\tau_c k_{\text{HC/O}_2} [\text{HC}]/[\text{O}_2]}{k_{\text{SCR-NO}} [\text{NO}]} \quad (1)$$

where SCR is a reference subscript which pertains to the carbonaceous SC reductant, $k_{\text{HC/O}_2}$ the rate constant for the deposition process and $k_{\text{SCR-NO}}$ for the reduction process. Two other factors are probably involved in the rapid increase of τ_R with temperature: an increasing preference of the reductant-forming reactions over the others (e.g., pyrolysis and oxidative), and an improving sticking coefficient for the carbon particles on the wall. The effect of diffusion here would be minor since the temperature changes are small and the dependence is approximately of the form $T^{1/2}$.

Effect of Residence Time. The effect of τ_{res} on τ_R was studied at constant τ_c and initial species concentration as in Figure 5 where $T = 1501$ K, $\tau_c = 20$ min, and $[i\text{-C}_4\text{H}_{10}] = [\text{O}_2] = 0.4\%$. The duration of the SC reduction increases monotonically with τ_{res} at a rate certainly greater than linear. A theoretical basis for τ_R can be deduced from the basic relationship

$$\tau_R = \frac{C_x}{-\frac{dC_x}{dt}_R} \quad (2)$$

where C_x is the amount of SC reductant deposited, and the subscript R refers to the final NO reduction process. Then since

$$C_x = \tau_c V \int_0^{\tau_{res}} \frac{d[C_n]_g}{dt} dt \quad (3)$$

where τ_c = duration of deposition, V is the volume flow rate, $[C_n]_g$ is the molar concentration (mass/cm³)/(12 n) of carbonaceous (SCR) particles of average number of C-atoms, n , formed and suspended in the gas phase (and eventually deposited), and

$$-\frac{dC_x}{dt}_R = \tau_R \dot{V} \frac{[\text{NO}]_f - [\text{NO}]_i}{\tau_{res}} \quad (4)$$

therefore

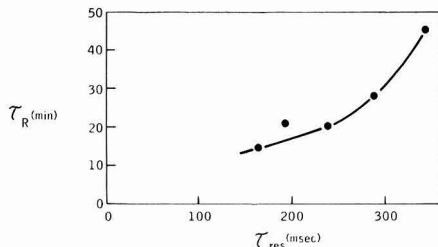


Figure 5. Duration of nitric oxide reduction as a function of residence time (τ_{res})

$T = 1501$ K; $\tau_c = 20$ min; $[i\text{-C}_4\text{H}_{10}] = [\text{O}_2] = 0.4\%$ and $[\text{NO}]_i \approx 1000$ ppm in N_2

$$\tau_R = \frac{\tau_c \tau_{res} \int_0^{\tau_{res}} \frac{d[C_n]_g}{dt} dt}{\tau_R (-\Delta[\text{NO}])} \quad (5)$$

Clearly, τ_R will vary at a power of τ_{res} greater than one in the integrated equation, in line with the data.

Chemical Effects: $[\text{O}_2]/[\text{HC}]$ Ratio and Addition of CO_2 and CO . The most significant chemical parameter in the homogeneous reduction of NO by HC- O_2 mixtures is the $[\text{O}_2]/[\text{HC}]$ ratio. It is also important in the SCR mode as shown in Figure 6 where τ_R decreases linearly with R_3 . Below $R_3 = 0.75$, uncertainty is introduced by excessive soot formation as indicated by the error bar. This behavior is analogous to the NO vs. $[\text{O}_2]/[\text{HC}]$ relationship for the gas-phase reduction of NO by HC- O_2 mixtures (1). There, on the lean side of the curve minimum, we also find that decreasing $[\text{O}_2]/[\text{HC}]$ promotes reduction. However, a more logical comparison here would be where $[\text{NO}]_f/[\text{NO}]_i$ is considered, rather than τ_R as we shall see later.

Pertinent to considerations of this phenomenon as a means of reducing NO in exhaust effluents is the effect of CO_2 and CO. When 13% CO_2 plus 1% CO are added, the result is essentially an inhibitory one for many conditions, but there still remains an effective (say over 70%) range for reduction. In the 1400 K range, τ_R is reduced by $\sim 1/2$, but at 1360 K, conditions can be found (e.g., $R_3 = 0.25$, $\tau_c = 20$ min) where $\tau_R = 35$ min. Below 1360 K the SCR efficiency falls off. It appears that part of the reason for high-temperature failure is oxidation of the carbonaceous reductant by the CO_2 . This is also true for the gas-phase process.

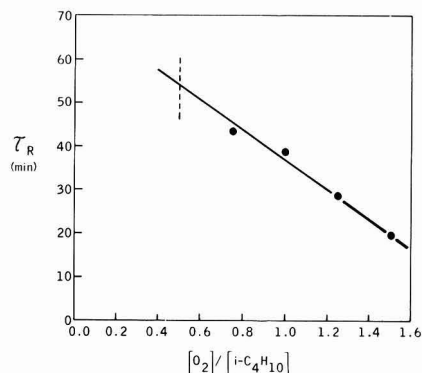


Figure 6. Duration of nitric oxide reduction (τ_R) as a function of $[\text{O}_2]/[i\text{-C}_4\text{H}_{10}]$ ratio

$T = 1493$ K; $\tau_{res} = 192$ ms; $[i\text{-C}_4\text{H}_{10}] = 0.4\%$, and $[\text{NO}]_i \approx 1000$ ppm in N_2

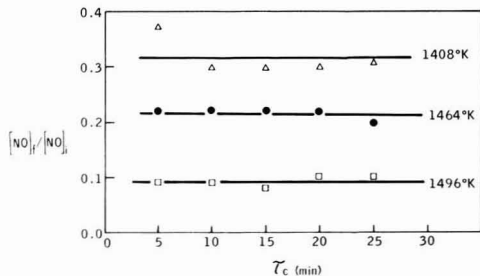


Figure 7. Maximum nitric oxide reduction as a function of conditioning time (τ_c)

$\tau_{res} = 190$ ms; $[i-C_4H_{10}] = [O_2] = 0.4\%$; $[NO]_i = 1000$ ppm in N_2

Factors Affecting Extent of NO Reduction. For most of the data discussed herein, the NO-time curves are of the type shown in Figures 1 and 2, and $[NO]_f/[NO]_i$ is taken as that corresponding to the minimum value attained. There appears to be 6 or so min involved in reaching the minimum, after HC- O_2 shut-off. Part of this time is due to simple flow-lag, but it is not clear what is involved in the remainder of that time. One possibility is that structural changes, both physical and chemical, are taking place in the SC reductant as reaction proceeds.

Effect of Conditioning Time. The principal result of depositing more reductant (longer τ_c) should be one of yielding a longer τ_R as we have already seen. Thus, for a given τ_{res} and T , there should be no reason to achieve greater NO reduction by increasing τ_c . This is borne out by the data of Figure 7 where $\Delta(NO)$ is independent of τ_c for a given temperature and τ_{res} , so that the reactivity of the reductant laid down must be essentially uniform with time.

Temperature Dependence. For a given type of reductant and τ_{res} , the dependence of the extent of reduction, $[NO]_f/[NO]_i$ on temperature should be representative of the chemical kinetics. This dependence is exemplified by the data of Figure 8. The reduction is fully 90% at the highest temperature (1500 K), but even this can be improved upon, as we shall see, by the use of longer τ_{res} . Virtually no HCN (<1 ppm) is produced here.

Dependence on $[O_2]/[i-C_4H_{10}]$ Ratio. In a previous section, it was found that τ_R is linear with R_3 . However, it was pointed out that R_3 's effect on $[NO]_f/[NO]_i$ would make for a more rational comparison with the gas-phase reduction reaction. Two curves of this type are shown in Figure 9. Just as was the case with the gas-phase process (1), it is clear here that the more effective SC reductant is produced by a higher $[O_2]/[HC]$ ratio. In addition, the data imply a preferred C—H—O composition and atom orientation for the SC reductant which depends in turn on the reactant ratio. Although other hy-

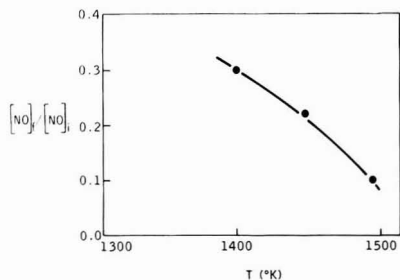


Figure 8. Nitric oxide reduction as a function of temperature
 $\tau_{res} = 190$ ms; $\tau_c = 30$ min; $[i-C_4H_{10}] = [O_2] = 0.4\%$; $[NO]_i \approx 1000$ ppm in N_2

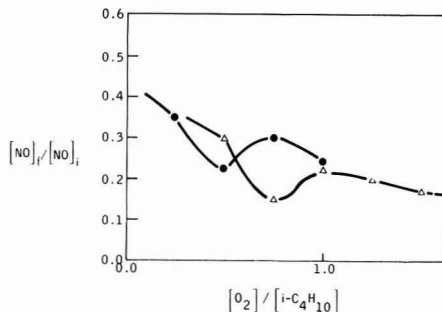


Figure 9. Nitric oxide reduction as a function of $[O_2]/[i-C_4H_{10}]$ ratio
●: $T = 1443$ K; Δ : $T = 1493$ K; $\tau_{res} = 180$ – 192 ms; $\tau_c = 20$ min; $[i-C_4H_{10}] = 0.4\%$; $[NO]_i \approx 1000$ ppm in N_2

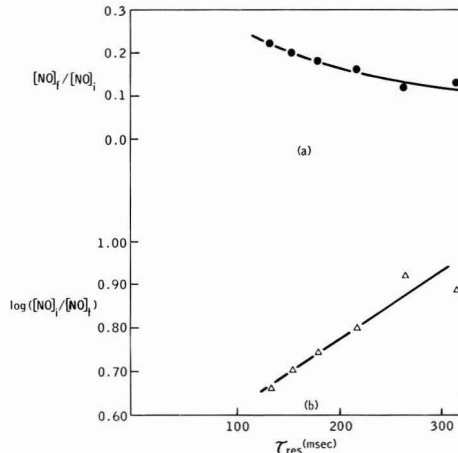


Figure 10. Nitric oxide reduction (a) and log of reduction (b) as a function of residence time (τ_{res})

$T = 1464$ K; $\tau_c = 20$ min; $[i-C_4H_{10}] = [O_2] = 0.4\%$; $[NO]_i \approx 1000$ ppm in N_2

drocarbons were not tried, one would expect specific effects peculiar to a given HC as in the gas-phase phenomena (1), but modified by the effect of HC structure on solid-carbon formation.

Chemical Rate Data. It was feasible to make a series of coherent measurements in which τ_{res} was changed at constant temperature and τ_c . The residence times were varied from 100 to 300 ms (flow rates from 9 to 4 L m^{-1}) for each set of NO reduction conditions, but the conditioning process was always carried out at 7 L m^{-1} to maintain a constant deposit of SC reductant at a given temperature. The results of a typical series at 1464 K are shown in Figure 10a which, interpreted in conjunction with the implications of Figure 7, indicates that the extent of reduction ($[NO]_f/[NO]_i$) depends only on the chemical kinetics and not on the amount (i.e., thickness) of SC reductant deposited.

If one assumes a first-order surface reaction for the NO

$$-d \frac{[NO]}{dt} = k_{SCR-NO}[NO]$$

and constant reactivity at the surface (until the SCR is completely gone), then

$$[NO]_f = [NO]_i e^{-k_{SCR-NO} \tau}$$

If $\log([NO]_f/[NO]_i)$ is plotted as a function of τ_{res} , the curve of Figure 10b results, so that it would appear that the reaction is close to first order in $[NO]$.

Table I. Nitric Oxide Reduction in Engine Exhaust by Heterogeneous SCR Mode^a

Mode	RPM	IMAP	A/F	T _{ex} , K	ppm		-Δ[NO], %	
					[NO] _i	[NO] _f		
1)	2399	24.2	14.3	1315	1765	1765	(No injection)	
2)	2402	24.1	14.3	1290	1765	336	81	
3)	2408	24.0	14.3	1370	1765	75	96	
1)	1900	20	14.8	1284	1714	1714	(No injection)	
2)	...	Injection not needed (SCRM already present)						
3)	1900	20	14.8	1284	1714	155	91	

^a Engine: 1970 Ford 302 CID V-8; compression ratio, 9.5. Operating modes as follows: 1) normal NO emission without HC-O₂ injection, 2) homogeneous gas-phase reduction by HC-O₂ injection, and 3) heterogeneous SCR mode (no HC-O₂ injection).

Although a small temperature range and many other variables are involved, as discussed under temperature dependence, it is of interest to calculate an activation energy. This yields an $E_a = 34\,000\text{ cal mol}^{-1}$ for data at two temperatures, 1408 and 1464 K, which is not too unlikely for a process in which a C—ON bond is formed on a carbon surface and an NO bond broken subsequently.

Diffusion Limitations and Automotive Application

Tests. Accurate calculations of the role of diffusion in this complex situation are not presently feasible, but estimations indicate that in the range of 50–80% of the NO molecules can reach the wall during typical residence times (which are compatible with auto exhaust manifold reactors). Since as much as 83% of the carbon originally in the HC gas has been observed to reduce NO after conversion to SC reductant it is not implausible that with higher surface areas (e.g., packed beds) a possibility for automotive application cannot be ruled out. Preliminary evidence for this SCR mode has been observed by Blair and the author during an automobile engine testing program (4) of the gas-phase reduction of NO by HC-O₂ mixtures. Here, inadvertent participation of this heterogeneous SCR mode took place. The SCRM data are shown in Table I, in which A/F is the air/fuel ratio, IMAP the intake manifold absolute pressure (in. Hg), and T_{ex} is the exhaust temperature between the exhaust valve and the reactor just downstream of it. Note that both of these SCR mode manifestations were going strong after approximately 1/2 h, when they were ended intentionally due to time limitations, by air additions to the reactor.

Prior to these measurements, 4.1 SCFM of air and 0.33 SCFM of ethane had been injected intermittently into the exhaust, just upstream of the reactor, over a period of several hours and then had been discontinued for a short period of time. Approximately 30 ppm HCN were present in the second test after correction for the ~10 ppm HCN normally present (4). This HCN would be finally oxidized to residual CO and NO along with oxidation of the CO and HC in any practical situation.

What constitutes the practical conditions necessary for this potential use of the SCR mode is unknown at present, but it is important to realize that the residence times are indeed compatible with auto exhaust manifold reactors. Several speculative possibilities have already been suggested, such as running two exhaust reactors in tandem (one being condi-

Table II. Localization of SCRM Activity with Ceramic Inserts^a

Insert removed	[NO], ppm	τ _R , min	Wt %			
			C	H	N	O
None	380	23.5				
A	380	21	90.2	2.8	1.2	4.7
B	380	16.5	86.3	1.9	2.2	7.1
C	580	16	95	0.5	0.7	8.54
D	No	0	98.4	0.9	0.7	...
SCRM						

^a [NO]_i = 1150 ppm, T_{gas} = 1451 K.

tioned, while the other acts as the SC reductant); maintaining a carefully balanced [O₂]/[HC] ratio so that a steady-state supply of SC reductant is maintained; or using a replaceable SCR-packed reactor, keeping in mind that a lightly packed 90 cm × 10 cm i.d. cylinder will last roughly 35 000 miles if removing 200 ppm of NO from a regular-sized automobile.

Isolation and Nature of Self-Contained Reductant. The location and identity of the substance responsible for the heterogeneous reduction process were investigated through the use of a number of 6-in.-long ceramic tubes or inserts of reactor-tube mullite. Their o.d. was almost that of the i.d. of the reactor (3/4 in.), and the wall thickness close to 1/16 in. The concept of the experiment was to provide readily removable walls that would substitute for the normal reactor walls in catching SC reductant.

The experiment was carried out by first placing four of these inserts (A, B, C, and D) contiguously, in the main reactor tube as shown in Figure 11. Then by preconditioning and establishing stable SCRM conditions in conjunction with a program of insert exchange, it was possible to ascertain the contribution made by reducing material in each segment of the reactor. (A more detailed account of this and other experimental procedures described herein is available as ref. 5.)

Table II shows the net successive effect of removing the SCRM contribution of each insert in turn. Thus, the contribution of A is small, while B's removal causes the τ_R to decrease from 21 to 16.5 min. The removal of C is important and causes the [NO] level to rise significantly.

Finally, the removal of D is fully fatal to the SCR mode, indicating that the SCRM's performance for 16.5 min at 580 ppmNO is almost completely dependent on the reducing material in D. Thus, the material responsible for most of the SCRM effects forms and reacts most effectively in the hottest part of the furnace.

The material in each insert was analyzed for C, H, N, and O with results as shown in Table II (averages of two complete experiments). As expected, the SC reductant is predominantly carbon, and if there is any trend, the more active material is

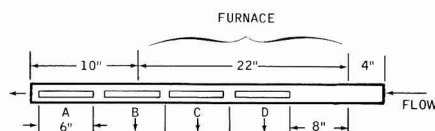


Figure 11. Schematic drawing of furnace showing location of inserts relative to furnace dimensions

higher in carbon and lower in hydrogen and nitrogen. (The percentages do not add up to 100 mainly because of inaccuracies in the neutron activation analyses of oxygen.) A repeat experiment on SCR mode localization showed identical trends in $[\text{NO}]$ and τ_R with reproducibility of the order of $\pm 20\%$.

Persistence of Activity. The conditions and their duration under which the reducing potential of the SCR mode could survive were measured by means of the four inserts previously described. Freshly prepared SC reductant lost about 60% of τ_R and only 70 ppm reducing ability if kept in a desiccator for 5 h and returned to position C and D, but became inactive at A and B (see Figure 11). However, fresh SC reductant left in the open air for the same time and replaced in the furnace exhibited an erratic SCR mode and lost more than 190 ppm of its reducing ability.

Electron Microscopic Study of SC Reductant. To study the physical nature and morphology of the activated carbonaceous reductant, an electron microscopic examination of the material in the inserts was carried out by Prestridge (6). Figure 12 is representative of the obtained electron micrographs which show that the reducing carbon is amorphous, nongraphitic, and extremely porous with a high surface-to-weight ratio. These facts and others (6) all point to a pyrolytic type of carbonaceous material formed through an intermediate stage of oxygenated aromatics involving C—H—O free radicals. The significant percentages of oxygen (along with N and H), as seen in Table II, are in line with the hypothesis (6) that functional groups such as quinones and hydroquinones are active at the surface. This provides an explanation for the consistent observation that the SCR mode is delayed several minutes after HC—O₂ flow is discontinued, since time will be required for the desorption of species blocking the critical functional groups.



Figure 12. Electron micrograph of carbonaceous reductant from furnace insert D (see Figure 1). Magnification = 100 000X

Gas-Phase Products of SCR Mode Reaction. To determine whether significant amounts of fixed (and undesirable) nitrogen compounds (e.g., HCN) are formed from the NO-SCR reaction, in addition to N₂, gas chromatographic analyses were carried out. A complete material balance was in order, so that analyses were performed for N₂, HCN, CO, O₂, and CO₂, using He as the diluent. The HCN was measured by the gas chromatographic method previously developed (7).

Three separate determinations were carried out at 1400 and 1450 K by creating the SCR mode with $\tau_c = 30$, using a mixture of 0.4% *i*-C₄H₁₀ and 0.4% O₂. After the principal regime of the SCR mode, ($\tau_r = 10.5$ min) had begun, a portion of the gas flow was diverted to the GC for sampling. In each of three experiments all (within $\pm 1\%$) of the N from the NO reduced, appeared as N₂, with less than 1 ppm of HCN produced ($[\text{NO}]_i = 945$ ppm; $[\text{NO}]_f = 195$ ppm, for the case of the first experiment). Also in the first 1400 K experiment, 92.4% of the O from the NO reduced, appeared as CO, 4.3% as CO₂, and 3.3% as O₂. The total initial $[\text{N}]$ or $[\text{O}]$ was 945 ppm and total analyzed products as $[\text{N}] = 951$ ppm and $[\text{O}] 941$ ppm; the other experiments also provided satisfactory balances (details of these experiments are available in ref. 5).

In summary, one can say that the SCR mode reduction proceeds cleanly for the most part in producing N₂ with a minimal amount of pollutants such as N₂O and HCN. The O₂ is an interesting side product and may be formed by catalytic decomposition of the NO on the surface and/or by evolution from the surface species themselves.

Conclusions

The self-contained reductant mode is a new technique for reducing nitric oxide heterogeneously from effluent-type mixtures, at temperatures higher than approximately 1300 K. It provides an efficient, carbonaceous reducing material directly on a ceramic (aut al) reactor wall by means of an initially gas-phase conditioning reaction between hydrocarbon and oxygen. A number of quantitative relationships have been determined and are summarized below.

At constant temperature the duration of reduction, τ_R , increases linearly with the conditioning time, τ_c , and decreases linearly with the $[\text{O}_2]/[\text{HC}]$ ratio. And for a given τ_c , τ_R increases more rapidly than linearly, with temperature and with residence time, τ_{res} .

The fraction of NO remaining, $[\text{NO}]_f/[\text{NO}]_i$, is independent of τ_c but decreases significantly with increasing temperature (0.05 for $T > 1500$ K) and with decreasing values of the $[\text{O}_2]/[\text{HC}]$ ratio. Data for $[\text{NO}]_f/[\text{NO}]_i$ as a function of τ_{res} indicate the reaction is first order in $[\text{NO}]$.

Engine exhaust tests for gas-phase NO reduction by HC—O₂ mixtures resulted in unplanned but impressive manifestations of the SCR mode, to the extent of 90–95% NO reduction.

The carbonaceous material responsible for the SCR mode NO reduction is a very high surface area, pyrolytic carbon containing a total of approximately 10% by weight, of oxygen, hydrogen, and nitrogen. The only nitrogen-containing product is N₂. The principal carbon-containing product is CO along with only small amounts of CO₂ and O₂. Accurate chemical material balances show that all species have been taken into account.

Acknowledgment

The author expresses his gratitude for the skillful and meticulous experimental efforts of this program as carried out by James J. Chludzinski, Jr., and initially by Raul Acosta.

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NOTES

Nocturnal Boundary-Layer Wind Maxima and the Problem of Wind Power Assessment

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■ High-resolution measurements of wind profiles collected over central Illinois indicate that nocturnal, low-level wind maxima occur more frequently than previously supposed. Since the periodic contributions of these circulations have been neglected, wind power potentially available over the central U.S. has probably been underestimated, especially in the case of surveys that have used simple, power-law profiles. An alternative method of profile representation appropriate to stability conditions characteristic of nocturnal wind maxima is reviewed, and it is suggested that the strong wind shears associated with these phenomena may present a special hazard to the long rotor blades of large, horizontal axis wind energy conversion systems.

The uncritical use of simplified wind profile representations for wind power assessment suggests a need for improved communication between engineers and boundary-layer meteorologists. In particular, inherently limited, empirical "power laws" have frequently been used to represent average vertical distributions of wind speed in national wind energy estimates (1, 2). Even atmospheric scientists are sometimes tempted to use these simple, analytically convenient relations (3). But power-law profiles can be misleading, especially when winds in the lower atmosphere have been partially released from the constraints of surface friction by the formation of strong, stable temperature gradients near the ground.

\bar{V}_h is the average wind speed measured at an arbitrary reference height h . Typically, the height selected for wind power assessment is the standard 10-m level recommended for climatological data collections.

Based upon a formula for fluid resistance in pipe flow given more than 60 years ago by Blasius (4), the power law often appears in a familiar form as "the seventh-root profile", so called because $p = 1/7$ fits flow distributions observed over flat plates in the laboratory. Almost an equal number of years ago, wind profiles measured in well-mixed conditions were also found to correspond with the one-seventh power distribution (5). But in general, the magnitude of the exponent p required to fit a power law to a particular set of wind data is a function of both the roughness of the surface over which the observations were made and the atmospheric stability that prevailed at the time. Thus, in deep, well-mixed flows of near-neutral or slightly unstable stratification, p ranges from 0.1 for winds measured over smooth water surfaces to 0.4 for profiles observed over very rough terrain (6). On the other hand, a similar range of exponent values (namely, $0.14 \leq p \leq 0.50$) will here be shown to be required to fit power laws to wind profiles measured over a single, relatively smooth site in thermal stratifications that ranged from well-mixed, unstable conditions by day to strong, stably stratified conditions at night. Unfortunately, no rational procedure has been found for predicting the value of this exponent from the external parameters, that is, from the surface roughness and stability conditions.

One engineering application in which power-law relations have been used successfully is the estimation of wind forces on buildings (6). In these cases, interest centers on strong winds conveniently maintained in the well-mixed conditions that favor simple profiles by the turbulence generated when air moves rapidly over rough, urban terrain. Indeed, this successful application of the power law to an engineering problem may have contributed to the tendency for wind power analysts to adopt the simplified profile relations. But with average winds over ordinary terrain, deep well-mixed conditions usually prevail for only a few hours during the middle of sunny days. To represent wind distributions over such sites at other times, the choice of a value for p can only be based on experience; apparently that experience has seldom included the low-level wind maxima considered here.

Momentum Decoupled Winds

Late in the afternoon stable temperature gradients begin

Improved wind profile equations perfected in recent years are capable of simulating some features of these "momentum-decoupled" conditions over a useful range of heights. More importantly, these newer relations are scaled in terms of the fundamental meteorological factors that control the vertical distribution of winds in the lower atmosphere, namely, surface roughness and the turbulent fluxes of momentum and heat. In contrast, power-law profile relations are essentially empirical in nature, and little general understanding of the dynamics involved in the distribution of winds above the ground is contributed to an atmospheric analysis when one of these simplified relations is employed.

Power-Law Profile

Power-law profile relations are of the form

$$(\bar{V}_z/\bar{V}_h) = (z/h)^p$$

where \bar{V}_z represents the average wind speed at height z , and

to form near the surface when the steadily declining supply of incoming radiation from the setting sun is no longer able to balance the outgoing components of the surface thermal energy balance. When this occurs in fairly light winds over a relatively smooth surface, the already weak turbulent mixing in the lowest layers is soon suppressed, and as a result frictional coupling associated with the exchange of momentum between the moving air and the ground is sharply reduced. Once decoupled in this way, winds previously restrained by friction are free to accelerate in response to existing pressure gradients; in fact, some overshooting takes place as the flow attempts to establish a new balance with inertial forces, and extreme departures from simple wind profiles occur.

Over all but the roughest terrain, some degree of decoupling takes place virtually every night during the stably stratified phase of the boundary layer's regular diurnal cycle. The phenomenon is less pronounced over water where initial frictional restraints are small and the surface heat budget is dominated by heat transferred from below. Strongest manifestations develop over land with favorable combinations of relatively smooth terrain, light to moderate surface winds in the late afternoon, and clear evening skies that permit unrestricted radiative cooling of the surface.

The mechanism outlined above follows Blackadar's 1957 explanation of the formation of nocturnal low-level wind maxima through momentum decoupling and inertial oscillation (7). Other mechanisms have been proposed (8, 9), but the observations described here best fit the Blackadar model.

The frequency and geographical distribution of low-level jets have been summarized by Bonner (10) who examined two years of winds aloft data from 47 U.S. radiosonde stations but did not find that nocturnal maxima occurred over Illinois as often as suggested by the present study. However, the standard observations used were taken only twice a day; then too, wind speeds were reported at only four levels below 1 km, namely, the surface, 150, 300, and 500 m. These limitations to data resolution and a minimum velocity criterion of 12 m s^{-1} adopted by Bonner to screen the data for "jet" occurrences, probably excluded all but the very strongest cases of decoupled winds considered here. In any event, high-resolution wind profiles recently measured over midwestern farmland (hourly observations at 25 levels below 1 km), as well as similar information collected in other atmospheric boundary-layer studies conducted over simple terrain (11, 12), suggest that nocturnal low-level wind maxima occur fairly frequently during the summer and fall over many extensive areas of relatively smooth terrain in middle latitudes.

Some Observed Profiles of Decoupled Winds

During two meteorological field experiments conducted by this laboratory in the summers of 1975 and 1976, low-level wind maxima were observed on 24 out of a total of 30 nights. In these studies, high-resolution measurements of wind profiles were made over the flat, nearly treeless corn and soybean fields of Sangamon County in central Illinois as part of a comprehensive investigation of the diurnal cycle of the structure of the lower atmosphere. Particular attention was paid to the periods of transition between daytime turbulent mixing and nocturnal turbulence suppression. In July and August of 1975 observations were made on 18 days for periods of 8 h across sunrise (0400–1200 CST); one year later similar measurements were made over the same site on 12 days for 6 h across sunset (1800–2400 CST).

Wind profiles above 30 m were measured hourly by tracking the horizontal movements of slowly rising balloons with two digitized theodolites located at either end of a 400-m-long baseline. Tracking information was transmitted by cables to a central station where it was recorded on magnetic tape once

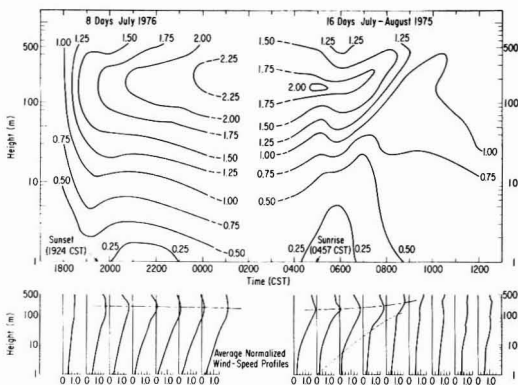


Figure 1. Time-height cross section of average, normalized winds observed in midsummer over Sangamon County, Illinois

Speeds expressed as approximate multiples of winds observed at 500 m in well-mixed, daytime conditions; sunset and sunrise times refer to middle of respective observation periods; average, normalized wind profiles shown at appropriate times below. Note growth and decay of relative wind maximum indicated by dashed line above 100 m; ascending line of short dashes following sunrise indicates increasing depth of mixed layer

each second by an automatic system especially developed for detailed atmospheric boundary-layer studies of this kind (13). Subsequent computer analysis averaged three successive balloon positions to smooth small tracking errors, and then calculated horizontal balloon displacements through successive atmospheric layers, 30 to 50 m deep. In 1975 winds near the ground were recorded by cup anemometers mounted 1, 3, and 7 m above the soybean crop; in 1976 only the 1-m wind was recorded over the bean field.

After eliminating six days of measurements because of thunderstorm or frontal activity, a total of 163 wind profiles recorded during 16 mornings in 1975 and 8 evenings in 1976 remained. These results are summarized in the time-height cross section of normalized average wind speeds presented in Figure 1. Here the day-to-day variations caused by changing pressure patterns have been reduced by dividing each measurement made on a given day by the wind speed recorded on that day at the 500-m level in well-mixed conditions. The latter circumstance was taken to be best represented in the available data by the last profile measured at 1200 CST during the morning runs and the first profile measured at 1800 CST for the evening runs. Since the isopleths of Figure 1 cannot quite be extrapolated from one set of data to the other without an amplitude adjustment of some 20%, normalization was evidently only partially effective. None the less, the evening and morning patterns obviously depict two stages in the evolution of an average boundary-layer circulation seen in two sets of data recorded one year apart.

Both the cross section and the hourly profiles of Figure 1 show a general acceleration of winds between 10 and 500 m that begins shortly after the onset of stable stratification in the surface layer, that is, during the hour preceding sunset. This initial phase is followed by a gradual formation of a relative wind speed maximum aloft which first appears near 200 m and then slowly sinks to 150 m. Winds at these levels gain strength throughout the night, and by sunrise the wind at 150 m has attained a speed twice that recorded the previous afternoon. The dissipation phase after 0500 CST is marked by an erosion of the wind maximum from below, a process at least partially associated with the growth of the convective mixed-layer following sunrise. During this stage the wind maximum weakens and rises, finally disappearing in mid-morning.

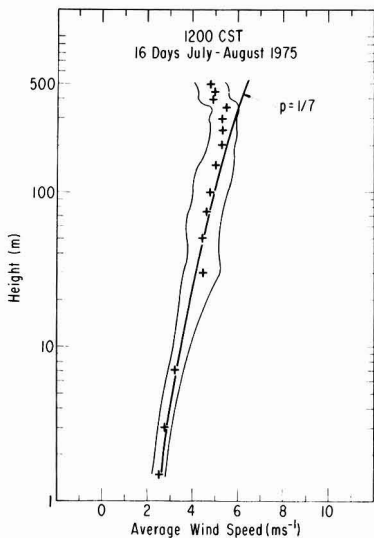


Figure 2. Average wind profile observed in well-mixed conditions at 1200 CST (16 days, 1975; not normalized)

Plus signs designate average values while envelope indicates 1 SD about these means; solid line represents seventh-root profile based on wind at $z = 10$ m

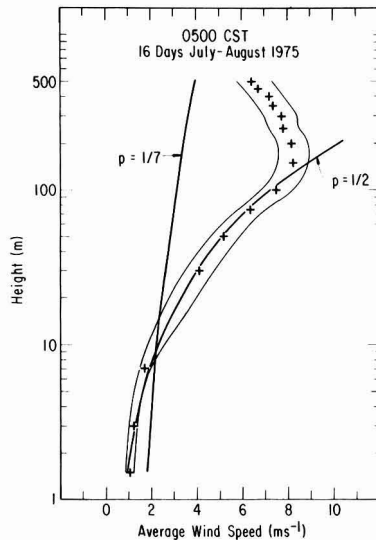


Figure 3. Average wind profile observed in decoupled conditions at 0500 CST (16 days, 1975; not normalized)

In addition to seventh-root profile, power-law profile with $p = 0.5$ is also shown (see discussion in text)

The dynamics of nocturnal wind maxima are fairly well-known, and their height, relative intensity, and time of occurrence are known to vary with a number of external factors, including latitude. Blackadar's model (loc. cit.) indicates that the maximum increase in wind speed at any level will be about twice the geostrophic departure observed in well-mixed conditions, that is, twice the difference between the actual wind speed observed at the time momentum decoupling first occurs and the speed predicted for that time by the local pressure gradient in the absence of friction. Similarly, maximum speed will be attained when the inertia circle is half completed, that is one-half inertial period after decoupling has initiated the acceleration. For winds over central Illinois near latitude 40° , this would be about 9.3 h after decoupling has released the boundary-layer flow. Since the measurements of Figure 1 were made in late July and early August when nights are about 9.5 h long, the maximum wind occurs near sunrise. The return phase of inertial oscillation should therefore take place during daylight hours, but apparently the details of this deceleration are obscured by the growth of the convectively mixed layer from below. At any rate, it should be emphasized that the sequence of decoupled wind profile development summarized in Figure 1 is only one example of what is probably a fairly common phenomenon; the sketch cannot be used as a nomogram for general assessments.

Figure 2 presents an unnormalized average of the sixteen 1200 CST profiles and compares this result with a seventh-root power-law distribution based on the 10-m wind speed. Note the comparatively small standard deviations that characterized the day-to-day variation of these wind profiles measured during the quasi-stagnant, convective regimes of typical midwestern summer weather. As expected in well-mixed conditions, agreement between the observed profile and the seventh-root, power-law distribution is quite good.

In marked contrast, a similar comparison to an unnormalized average of the 0500 CST profiles shown in Figure 3 illustrates the inability of a simple, seventh-root power law to represent the strong low-level shears that occur in fully decoupled conditions. Exponents in the range $0.20 \leq p \leq 0.25$

often used for wind power assessment (2) will not do much better since, as shown in the diagram, a power-law exponent of 0.5 would be required to fit the rapid increase of wind with height observed between 10 and 150 m. But, as noted earlier, there is no theoretical means whereby a value of p this large could have been predicted from the prevailing conditions of stability and site.

Similarity Theory and Limiting Linear Profile

A partial answer to the problem of representing wind profiles in strong stable stratifications may be found in an extension of the similarity theory of Monin and Obukhov (14) recently discussed by Hicks (15). Briefly, similarity analysis notes that in the lowest 10 or 20 m (that is, sufficiently near the surface for the fluxes of heat and momentum to be considered invariant with height), only two external factors determine the wind profile. These are the surface stress, usually expressed as the friction velocity u_* , and a height-dependent stability parameter z/L in which the factor L is the Monin-Obukhov length scale and the ratio essentially represents the relative rates at which the heat and momentum fluxes generate turbulence. Scaling wind profiles in terms of these factors defines the dimensionless wind shear function, ϕ_m :

$$\phi_m(z/L) \equiv (d\bar{V}/dz)(kz/u_*) \approx 1 + \alpha z/L$$

Here, the subscript m refers to the role of this function in momentum flux relations, $k \approx 0.4$ is the von Karman constant, and the expression on the far right represents the first term of a series expansion for which a value of the constant α can be determined by experiment. For the stable conditions of present interest, $\alpha \approx 5$ is appropriate for conditions ranging from slight to moderate stability. (The behavior of the ϕ_m function in unstable conditions is summarized in ref. 6.) Further, Hicks (loc. cit.) has found that once very strong stability sets in (conceivably, once momentum decoupling is fully established in the surface layer), the value of α decreases rather suddenly to about 0.8. We can thus assume $\alpha \approx 1$ in order to rewrite the ϕ_m function as an expression for wind shear in near-decoupled conditions:

$$d\bar{V}/dz = (u_s/k)(1/z + 1/L)$$

Clearly, when $z \gg L$ (Hicks suggests $z > 10L$), the second term in parentheses on the right becomes dominant, and the expression reduces to

$$d\bar{V}/dz \approx u_s/kL$$

Evidently, in stable conditions the dependence of wind shear on height becomes negligible above $z \approx 10L$, and the profile becomes linear.

Hicks examined winds recorded on a 16-m tower in very stable conditions ($L < 1$ m) and found linear profiles that began at elevations below 10 m. In the stably stratified pilot-balloon data summarized in Figure 3, the average profile approaches linearity above 30 m and is approximately linear from 50 to 100 m. This suggests that, on the average, L was 5 m or less. Of course, this interpretation ignores the fact that similarity theory ordinarily cannot be expected to apply at elevations above 10 or 20 m, that is, above the surface layer of constant flux. But conceivably, in the special circumstances of strong stability and complete decoupling, the weakened transfer properties of stability-suppressed turbulence may define a new layer of constant flux (essentially one of near-zero flux) through the entire depth of the regions of constant wind shear aloft.

Figure 3 supplies the data for a numerical example. Through the linear region from 50 to 100 m, we find $d\bar{V}/dz \approx 0.04 \text{ s}^{-1}$; substituting this value in the constant shear relation gives $u_s \approx L/60$. Finally, since the height at which the linear profile begins indicates $L \leq 5$ m, we obtain the estimate $u_s \leq 8 \text{ cm s}^{-1}$, a reasonable value for the average surface winds of only 1 m s^{-1} recorded at 0500 CST.

The converse of the foregoing procedure seems reasonable as well. That is, given measurements of u_s and L appropriate to strong, stably stratified conditions over a relatively smooth site, application of the linear profile relations would make it possible to estimate the wind shear aloft. With wind speeds measured at one upper level, say at $z \approx 10L$, approximate profiles could then be constructed to provide estimates of the additional wind power available in the lowest 100 m in decoupled conditions.

Obviously, more work needs to be done. But a theoretical framework exists, and additional measurements made in deep stably stratified atmospheric boundary-layers could improve present knowledge of the linear profile regime to a point where useful estimates of decoupled wind profiles might be made from a few measurements of the controlling, external parameters.

Conclusions

High-resolution wind-profile measurements made over midwestern farmland suggest that nocturnal low-level wind maxima occur more frequently than previously had been supposed. As a result, both the quantity and the reliability of wind power potentially available over the plains of the central U.S. may have been underestimated, especially when such estimates have been based on power-law profiles. Although there is no fully developed method to predict in detail the jet-like profiles that characterize the momentum-decoupled regime, an extension of surface boundary-layer similarity theory appears to offer a means whereby the strength of the large shears that occur below the wind maxima could be es-

timated from measurements of atmospheric stability and surface stress.

It is of interest to speculate on the effects these strong low-level wind shears might have on wind energy conversion installations themselves. In the case of horizontal axis machines for which rotors as large as 100 m in diameter have been proposed, the long blades required would probably experience severe mechanical strains as they alternately sweep through regions of higher and lower wind speed at the top and bottom of each rotation. On the other hand, small, vertical axis machines mounted on tall towers could tap a useful fraction of the additional energy available in the lower portion of nocturnal wind maxima aloft. Note that even at $z = 50$ m the normalized winds of Figure 1 exceed unity more than half the time; that is, during periods favoring decoupled conditions, more often than not the winds at 50 m exceed those found at 500 m in well-mixed regimes. It follows that when assessments are made of the wind energy potentially available over the farmlands and plains of the central United States, consideration should be given to the frequency, strength, and duration of nocturnal, low-level wind maxima.

Acknowledgment

The field expeditions that collected the data summarized here were carried out by members of the Atmospheric Physics Section, Radiological and Environmental Research Division, Argonne National Laboratory. This continuing investigation is one portion of the Multi-state Atmospheric Power Production Pollution Study (MAP³S) organized by the Division of Biomedical and Environmental Research, U.S. Energy Research and Development Administration, and was sponsored in part by the Midwest Interstate Sulfur Transformation and Transport program (MISTT) organized by the U.S. Environmental Protection Agency.

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Reexamination of Moisture Anomaly in Analysis of Peroxyacetyl Nitrate

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■ The effect of water vapor on the calibration of electron capture chromatographs for peroxyacetyl nitrate (PAN) was examined in response to conflicting reports of loss of sensitivity in dry mixtures. We observed such a consistent loss of sensitivity only in dry, acid-washed flasks. It was attributed to adsorption of PAN onto an active surface from this 140 ppb sample because a portion of the PAN could be recovered by adding water to the flask.

Holdren and Rasmussen (1) have reported the loss of sensitivity of electron capture detectors to low concentrations (≤ 100 ppb) of peroxyacetyl nitrate (PAN) at low humidities. In another paper, Nieboer and Van Ham (2) reported using a carrier gas that had been humidified to avoid this change in peak height. However, they presented no experimental evidence showing this anomaly. Lonneman (3) attempted to verify this loss of sensitivity in the USEPA laboratories, but was unable to do so and concluded that the results of Holdren and Rasmussen were "unique to their system". In correspondence accompanying Lonneman's paper, Holdren and Rasmussen cited a recommendation by one of us (E.R.S.) (4) that "air of normal humidity" be used for calibration. This might imply an effect of water on PAN sensitivity, although no such effect was claimed or reported. Ambient air measurements could be in error if the calibration mixture was used at a different humidity from that of the sample to be analyzed and if there were a "moisture anomaly". Since we have used this method to analyze PAN in air for many years, we reexamined this question with our instruments. Such an anomaly occurred only for calibration standards prepared in flasks that had been acid washed.

Experimental

Two different types of electron capture detectors were used in our studies. Direct current tritium detectors were used in a Wilkin's Instrument and Research PAN-680 gas chromatograph, and a Pulsed Current Mode Nickel-63 detector was used in a Hewlett-Packard Model 5750B gas chromatograph. The detectors were not heated for most experiments. Standard cylinder nitrogen was used as carrier gas for the direct current detector, and 5% methane in argon mixture was used in a pulsed current detector. Since Holdren and Rasmussen favored an interaction between column and sample as an explanation for their moisture anomaly, we tried three different columns. One (a three-year-old column), consisted of 5% carbowax 400 on chromosorb G, AW-DMCS (60-70 mesh). Newly prepared columns with 5 and 20% carbowax 400 on chromosorb G AW-DMCS (60-70 mesh) in 24 by 1/8 in. o.d. tubes were also tested. Samples of peroxyacetyl nitrate were prepared by the method described in ref. 4, that is, photolysis of ethyl nitrite vapor in oxygen in a 10-cm infrared gas cell. The formed concentrations of PAN were calculated from the infrared spectra using the absorbances given in ref. 4. This method yields about 140 mL of an oxygen-PAN mixture containing 200-400 ppm of PAN. These were diluted to the range of 10-800 ppb by transferring small samples into 2- or 20-L glass flasks previously filled with cylinder air. Different amounts of distilled water were then added to the dilute

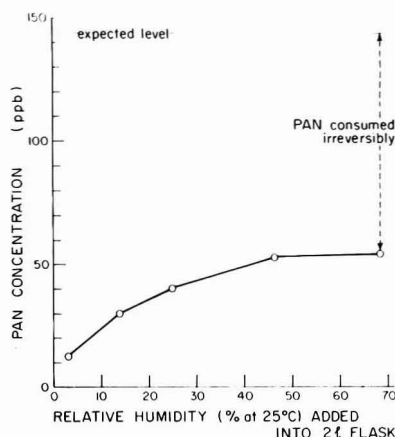


Figure 1. Desorption of PAN by addition of water to 2-L flask washed with 2 N HCl

PAN-air mixtures with microsyringes (5-150 μ L) to obtain relative humidities in the range of 10-60%. This was done before and after introduction of the PAN. These mixtures were then injected into the chromatograph using a six-port two-position gas sample valve with a 5-mL loop. PAN peaks were identified by sampling the gas through sodium hydroxide pellets that destroy the PAN by hydrolysis (4).

Results and Discussion

PAN concentrations ranging from 10 to 800 ppb were tested in various instruments under different conditions. The tritium direct current detectors invariably showed no humidity effect except in a few cases where 5-10% decrease in peak height was observed with 2-5% relative humidity. Peak heights decreased by a few percent per hour. With the instrument that used the Nickel-63 pulsed current detector, responses at low humidity (2-5%) were unstable, sometimes being only 30% up to 95% of the peak height shown by samples at 53% relative humidity. This occurred regardless of concentration, column, detector temperature, or pulsed duration in the detector. It is not clear whether this difference is a humidity effect on the detector, the column, or in the sampling valve. There was no clear difference in the moisture anomaly for the three columns with different liquid loadings and different histories even after a bake-out treatment. It was concluded that there was no important sample-column interaction in our experiments. All prior ambient air data from the Statewide Air Pollution Research Center have been obtained with tritium detectors; therefore, they should be subject to this uncertainty. We have not concluded that there is any inherent fault either in the Ni-63 detector or the instrument it was used in.

To test the effect of calibration flask surface activity, some of the 2-L flasks were washed with 2 N hydrogen chloride solution and then with water to obtain a greater surface activity. In these experiments a decrease of peak height of PAN was observed. At PAN concentrations lower than 100 ppb and at

relative humidities of 2–5%, the washed flask showed a complete disappearance of PAN as compared to unwashed flasks. Since the surface activity was not consistent from experiment to experiment, it was not possible to determine activity exactly. However, we can calculate that 100 ppb of PAN in a 2-L flask is equivalent to about 5×10^{15} molecules; if each molecule occupies a surface area of 0.2 nm^2 , just under 10 cm^3 are needed to adsorb the entire 100 ppb of PAN. The 2-L flasks used had a geometrical surface of about 1000 cm^2 ; therefore, there is plenty of geometrical surface to adsorb all the PAN for monolayer coverage. This is an attractive hypothesis because it accounts for the fact that only the lowest concentrations are affected. At high concentrations a small amount of loss to the walls would not be so readily apparent.

Holdren and Rasmussen reported that removal of a sample of 10 ppb of PAN prepared in dry air followed by humidification yielded a full response. They regarded this as evidence that the effect was not caused by the container surface. Our result for a similar experiment was just the opposite. A few microliters of water were added to the flask in which PAN was prepared in dry air. After allowing about an hour for the water to vaporize, the concentration had increased. Presumably, water caused the desorption of PAN from the dried flask surface. A typical experiment shown in Figure 1 was carried out using the instrument equipped with the tritium detector because of its less erratic behavior. Apparently, only a portion of the adsorbed PAN could be desorbed because the full

concentration was not recovered even at the highest humidities. If the flask was humidified before addition of the PAN, there was no loss of PAN. These observations can be accounted for by assuming that there are local active sites with a strong affinity for both PAN and water so that increasing of humidity causes desorption of the PAN and competitive adsorption of water molecules. If water is introduced in advance, the active sites are covered and PAN adsorption does not occur.

Since any of the equipment used for handling PAN has the potential for surface adsorption, such equipment should be selected and treated with care and also tested for the loss of PAN. Moist air should be used as a calibration medium, and humidification of carrier gas may be used as a preventive measure. Storage of either calibration mixtures or ambient air samples for any appreciable time is an uncertain procedure in the present state-of-the-art.

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INDUSTRY TRENDS

Neptune International Corp. has acquired Universal Engineered Systems, Inc. (Pleasanton, CA) for an undisclosed amount of cash. The acquired firm produces microprocessor-based control and telemetry systems.

DeZURIK (Sartell, MN), a unit of General Signal Corp., has acquired

Permascal Valve Corp. (Rochester, NY). Both companies make valves for power generation, paper, and many other industries.

General Electric has won a contract from the U.S. Dept. of Energy (DOE) for the preliminary design of a low-cost heliostat (solar reflector) aimed at

reducing solar electric generation costs.

Reynolds Aluminum has received the 1976 Governor's Environmental Quality Award for its recycled aluminum plant at Sheffield, AL.

Research-Cottrell has extended its line of lime-based units to complement the established double-loop limestone systems.

Union Carbide Corp.'s Linde Division will supply a PhoStrip phosphorus removal system for wastewater treatment at the Erie County-Southtowns Sewage Treatment Agency (NY).

Meteorology Research, Inc. (Altadena, CA) has formed an Industrial Air Quality Department to offer expertise and to quantify and solve problems in industrial air pollution.

Peabody Process Systems will design a desulfurization system for a pressurized coal gasifier at ERDA's Energy Research Center (Morgantown, WV).

The Carborundum Co.'s Pollution Control Division has a \$1.5 million contract from the City of Rochester, MN, to supply and install a baghouse fly ash emission control system for the city's North Broadway Power Plant.

Wyle Laboratories (El Segundo, CA) has won a \$669 000 aircraft noise reduction study contract from the Federal Aviation Administration.

Combustion Engineering, Inc. and Consumers Power Co., have reached a settlement of litigation between the firms regarding work at Consumers' nuclear power plant (Palisades).

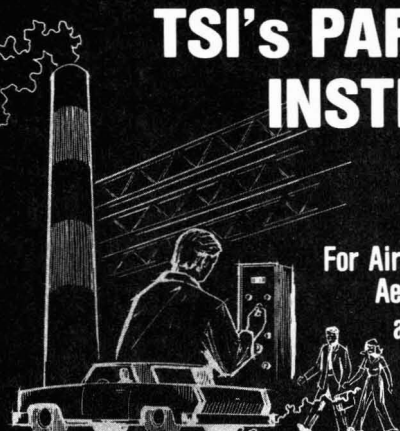
York Research Corp. (Stamford, CT) and Fred C. Hart Associates, Inc. (New York, NY) have a \$60 000 EPA contract for assistance in taking remedial action in instances of hazardous waste spills.

Ames Crosta Babcock Ltd. (England) will supply a 17-mgd potable water treatment (reverse osmosis) for the city of Riyadh, Saudi Arabia, under license from Ajax International Corp. (Santa Barbara, CA).

Lockheed Missiles & Space Co., Inc. (Huntsville, AL) is installing a solar

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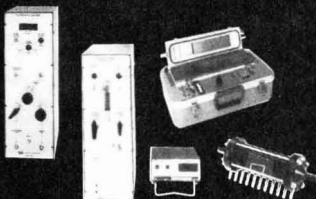


ELECTRICAL AEROSOL SIZE ANALYZER, Model 3030
 ... gives size and analog information for 0.003 to 1 micrometer aerosols in 10-diameter increments. Automatic operation and rugged construction make this instrument ideal for lab studies as well as airborne, mobile trailer and on-site applications.

ELECTROSTATIC CLASSIFIER, Model 3071
 ... used for production of highly monodisperse submicrometer aerosol from a polydisperse source. Also used for primary calibration of submicrometer particle size measuring instruments, filter testing or selective classification of particles for elemental analysis.


ELECTROSTATIC AEROSOL SAMPLER, Model 3100
 ... uniformly collects liquid or solid particles in the 0.02 to 10 micrometer range. Compact and portable. Collects unbiased samples on any flat substrate. Ideal for electron and optical microscope sampling.

DIFFUSION BATTERY, Model 3040
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CIRCLE 6 ON READER SERVICE CARD

heating system for Ulery Greenhouse Co. (Springfield, OH), under DOE funding, to prove technical/economic feasibility. It should furnish about 60% of greenhouse heating needs.

Combustion Equipment Associates, Inc. will provide a resource recovery facility to the City of Peabody, MA. The company processes ECO-FUEL II, a low-sulfur refuse-derived fossil-fuel substitute.

Permutit Co., Inc., now a subsidiary of Zurn Industries, received a Dept. of Interior contract worth \$150,000 to increase water recovery efficiency of pressure-driven membrane desalination systems using reverse osmosis/ion exchange.

Union Carbide has received the first "Clean Water Award" from the Izaak Walton League of America for its Marietta, OH, plant. The plant uses the "UNOX" activated sludge biological wastewater treatment developed by Union Carbide.

Andco Environmental Processes, Inc. (Buffalo, NY) has introduced a new Fluoride Removal system that will lower fluoride levels enough to meet EPA requirements for municipal drinking water, and for industrial wastewater.

Hittman Associates, Inc. (Columbia, MD) has a DOE contract to develop energy planning methodologies for use by community planners. This will include waste heat and energy utilization.

American Air Filter Co., Inc. will provide a second electrostatic precipitator system, valued at over \$5 million, for Big Rivers Electric Corp. (Henderson, KY). It will remove fly ash from a 240-MW unit.

Stone & Webster (Boston, MA) is developing design criteria for a standard coal-fired plant for 10 western utilities. Sulfur and ash will be taken into account.

Air Products and Chemicals, Inc., announced that it will supply two oxygen generators to the Passaic Valley (NJ) Sewerage Commission for what will be the largest oxygen generation complex in the world—480 tpd of oxygen; 6 tpd of liquid oxygen.

Solarex Corp. (Rockville, MD) will develop point- and line-focusing concentrator solar cells for DOE's Sandia Laboratories, pursuant to a \$287,540 contract. A commercial product development plan must also be delivered.

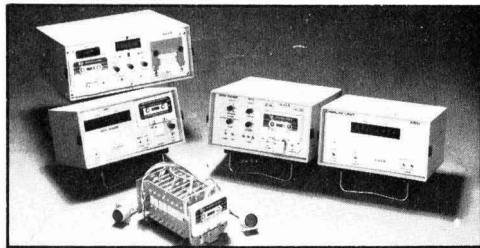
Martek, the specialist in environmental data acquisition, now offers the Series DAS, an economical, flexible data acquisition system to meet a wide range of applications and provide logging and retrieval of data from environmental instrumentation.

The heart of the Series DAS is the rugged, expandable DLS Data Logger which can record up to 99 analog or digital signals plus day and time of day, and can be operated on AC or DC power. The companion Model

Martek makes the difference in data acquisition.

DRS Data Reader features a digital LED display which permits visual reading of the tape while the information is simultaneously available at the output connectors for external data processors. The Model EDP Environmental Data Printer records—continuously or intermittently—up to 15 data signals and time of day on a magnetic tape cassette and/or digital paper printer.

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For the full story on the full line of Martek data acquisition systems, write to:



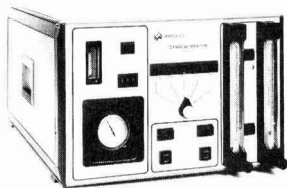
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Manufacturers of Environmental Instrumentation

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ES&T PRODUCTS



Gas analyzer calibrator

It generates and delivers gases in concentrations ranging from 0.0001 to more than 1000 ppm. Permeation chamber temperature is variable to 50 °C and controllable to within ± 0.05 °C. Flow is calibrated and stable to within 1% of each individual reading. Metronics 101

Plastic fume scrubber

The scrubber, available in fiberglass armored PVC and polypropylene, fiberglass armored Kynar or solid fiberglass, exhibits 99+% efficiency in capacities ranging from 500–35 000 cfm. A liquid recirculating sump reduces liquid consumption by up to 95% in most applications in both the vertical countercurrent and horizontal cross-flow models. Harrison Plastics 118

Anionic flocculant

Formulated to thicken and dewater mineral process slurries, the flocculant is especially useful in plants that have a variable pH. The product is said to show resistance to high shear conditions encountered in a centrifuge. Nalco Chemical 130

Process control module

The module is a digital controller that utilizes a microprocessor to combine controller, alarm outputs, totalizer, algorithms and auxiliary logic in one unit. Each microprocessor/module handles a single control group function. Robertshaw Controls 131

Pulse-jet filter

This high-pressure expansion filter reduces energy costs by virtue of its smaller baghouse size coupled with recirculation of cleaned warm air. The filters are available in sizes from 20 000 cfm to greater than 500 000 cfm. General Resource 132

Phenol analyzer

The device continuously monitors phenol in fresh or seawater and, as an

on-line instrument, it can be used to sample industrial plant wastewater. The system uses an UV analyzer that includes a single-sample cell and chopped beam, and dual wavelength electrooptical design. Teledyne Analytical Instruments 133

Digital thermometer

The portable model, for thermistor probes, has a range of -40 to $+140$ °C with 0.1 degree resolution over the entire range. The instrument features include automatic brightness control of display, dual function switch for continuous or intermittent operation, and automatic shut-off. Eltex 134

Organic contamination monitor

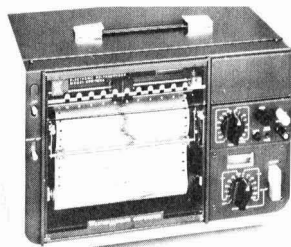
Measurement detection level is as low as 10 ppm. The monitor finds special application as a spill detector or organic contamination of boiler condensate return, feed water and other high-purity water supplies. Ionics 135

NO/NO_x analyzer

The instrument is capable of on-line measurement of NO and total oxides of nitrogen. Response time is less than 1 s to 90% full scale, and 2 s to 95% full scale. The instrument can be used in emissions monitoring of industrial and municipal incinerators. Environmental Tectonics 102

Fabric filter dust collectors

These collectors are designed to meet all low-volume dust collection requirements up to 15 000 cfm. The collectors are automatic and self-cleaning, and are available in 10 different sizes. Johnson-March 103

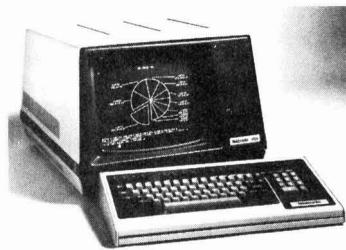


Potentiometric recorder

The recorder, which operates on AC or DC power or batteries, features 13 chart speeds, 16 input ranges and 1- or 2-pen recording. WeatherMeasure 104

Ammonia monitor

The portable monitor is designed for continuous monitoring of ammonia in the ambient air or workplace atmosphere. The unit has a range of 0–5 ppm full scale with a detectable limit of 0.05 ppm expandable to a full-scale range of 0–50 ppm. It will also analyze impinged samples. CEA Instruments 105



Computer display terminals

The 4025/4024 series were designed for the alphanumeric user who wanted to expand to graphics. The graphics terminals feature high resolution and high density graphics. Both the 4024 and 4025 are microprocessor-based terminals with local function capability. Both feature alphanumeric displays of 80 characters across with 34 lines. Tektronix 106

Flowthrough water sampler

The sampler is designed for periodic sampling from a continuous flow of water. At preselected times a self-cleaning solenoid valve is activated to divert a portion of the stream to the sample container. Sigmamotor 107

Alarm control

The sensor in this high-low alarm set-point controller is non-contacting, and operates on ultrasonic echo-return principles. Two alarm points are set directly on readout dials. Inventron Industries 111

Coagulant

This liquid polyelectrolyte coagulates suspended solids and colloidal solids in clarifiers and slurry thickeners. Nalco Chemical 109

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Oil in water analysis system

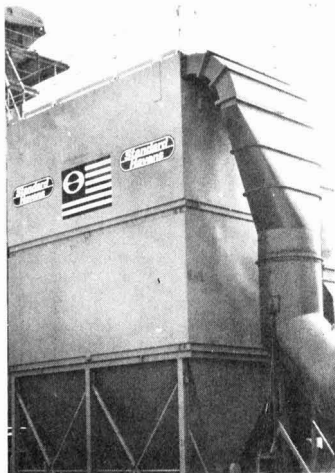
This dual wavelength photometric analyzer was developed for monitoring recycled cooling water, effluent from refineries and discharges from wastewater treatment plants. Variations of 0.1 ppm in process streams can be detected with an accuracy better than $\pm 2\%$. Teledyne Analytical Instruments **108**

Chlorine leak detector

By means of an electrochemical sensor that uses a gas-permeable membrane, the detector can measure chlorine gas concentrations as low as 1 ppm. The remote sensor can be located 100 ft away from its indicating control unit. Delta Scientific **113**

Pitch fume filter

This coke particle filter removes vapors, volatile fumes and other contaminants from an air stream. The filter design depends on temperature, pressure and particle size of the contaminant being removed. Union Carbide **114**



Baghouse

This reverse pulse baghouse with 19 ft bags comes in 21 different sizes—from 5208 sq ft to 31 248 sq ft of cloth area. The manufacturer claims that the number of bags, solenoids and other components are less than those for other baghouses of standard dimensions. Standard Havens **110**

Reverse osmosis equipment

The complete system includes a pre-filter, rotary vane pump, reverse osmosis modules, pressure gauges and conductivity light. Salt rejection is 90–98% of total dissolved solids. Four sizes are available: 1.6, 7.1, 15.5 and 21.3 gal/h. Ion Exchange Products **127**

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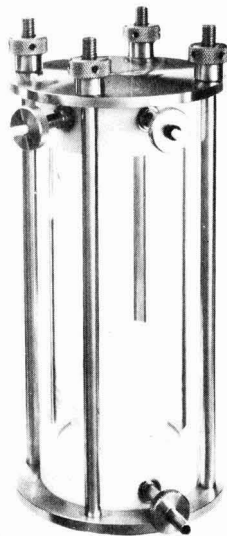
- wetted surfaces in glass and PTFE
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- takes integrated samples
- eliminates the contamination problem
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- can be handled by unskilled personnel

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- pesticides, herbicides (DDT, lindan, etc. etc.)

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For field use an in situ attachment device is available,



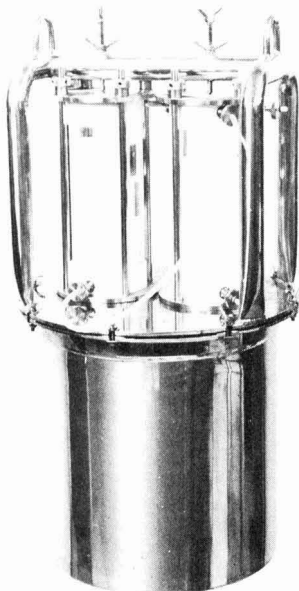
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LITERATURE

Safety supplies. Catalog lists many items applicable to workplace health/safety in accordance with OSHA regulations. Certain items can be purchased or rented. Interex Corp. **151**

Plastic controls. Composite catalog lists full line of resistant plastic valves for corrosive and ultra-pure liquid applications. Acid and waste pumping is also featured. Plast-O-Matic Valves, Inc. **152**

Vacuum pump. Brochure describes the benefits of a new non-polluting, energy-saving vacuum pump for use in the chemical industry. Can work at pressures of less than 1 torr. Busch, Inc. **153**

Reverse osmosis. Bulletin PB843 tells about a high-volume reverse osmosis water purification system for production of 800-1600 gpd. Capital/operating costs are much lower than those of distillation. Millipore Corp. **154**

Liquid filtration. Catalog lists many products for liquid filtration with applications in hydrocyclones, sump cleaners, dragouts, and other uses. Polyclon, Inc. **155**

Solar energy. Bulletin SE 1-76 describes a solar collector glazing material that is more efficient and cost-effective than other plastics or glass, according to the company. Vistron Corp. **156**

Boiler service. Brochure PSG-5194 describes a unique capability to establish/support local maintenance/service centers for fossil and nuclear power plants. Combustion Engineering, Inc. **157**

Air monitoring. Company journal, "Environmental Measurements", tells about a broadening of the company's consulting capabilities in air pollution monitoring. Environmental Measurements, Inc. **158**

Water clarification. Bulletin BVK101 describes a centrifugal clarifier that uses a new concept to remove up to 97% of suspended solids from municipal and industrial wastewaters. More compact, less costly. Bird Machine Co., Inc. **159**

Filter leaves. Bulletin No. 734 describes filter leaves with unique design that permit a thicker filter cake buildup. The leaves can be rescreened. Newark Wire Cloth Co. **160**

Precipitators. Bulletin ES-1-216 describes electrostatic precipitator applications for electric utility coal-fired boilers. Design/construction capabilities are featured. American Air Filter Co., Inc. **161**

Purified pesticides. "Pesticides Catalog No. 78" lists nearly 400 purified pesticides for use in pesticide research/analysis. Fungicides, insecticides, herbicides, and plant growth controllers are included. Chem Service, Inc. **162**

Dust collector. Bulletin P-750 provides unit selection, construction, and dimension data for pulse jet dust collector able to handle high gas velocities. Range 114-9437 ft²; 16-1000 bag units. Buffalo Forge Co. **163**

Centrifuges. Brochure, "Decanter Centrifuges", presents "run-down" on applications, including waste treatment, oil separation, paper mill waste recovery, and others. The De Laval Separator Co. **164**

Meters and testers. Catalog 77A describes expanded line of instruments, such as pH meters, chlorine testers, turbidimeters, soil testers, colony counters, and the like. Hellige, Inc. **165**

Environmental control. Brochure, "The Environment and Combustion Engineering", lists 35 products/services, and features recognition of problems before they happen. Combustion Engineering, Inc. **166**

Drinking water coolers. Brochure on mobile drinking water coolers describes this equipment, which contains drinking bubblers with filter purifiers. Environmental Tectonics Corp. **167**

Chromatography. Bulletin 113-77 explains why pellicular (superficially porous) column packings are still important for liquid chromatography. A selection guide is included. WHAT-MAN INC. **168**

Precipitator. Brochure RC-1600 describes acid-resistant fiberglass reinforced plastic (FRP) electrostatic precipitator. Specially designed for pulp/paper, chemical/metallurgical, pigments, spray drying, and steel applications. Research-Cottrell **171**

Confined area entry. Brochure discusses atmosphere of confined spaces, and covers toxic gas detection, oxygen deficiencies, combustible gases, and protective devices. BioMarine Industries, Inc. **182**

Mist elimination. Bulletin KJV-1 features a unique non-plugging mist eliminator. Koch Engineering Co. **190**

Fuel savings. Bulletin tells how 10-35% fuel savings can be achieved by modernizing combustion control systems. Thermal equipment, Inc. **191**

Dust control. Article portfolio explains how wet suppression methods efficiently control dust in many industrial and mining operations. Johnson-March Corp. **193**

Water testing. Water and Wastewater Manual covers over 30 EPA- and APHA-approved methods for chemical/microbiological tests on drinking water and wastewater, with glossary. Sargent-Welch Scientific Co. **195**

Storm drains. Brochure TRX-4 gives properties, applications, and other pertinent details on Transite storm drain pipes made of asbestos/cement. Broad array of applications. Johns-Manville **196**

Oil spill monitors. Symposium paper reprint (1977 Oil Spill Conference, New Orleans, La.) lists current commercial applications of non-contact oil spill monitors in refineries and manufacturing plants. Wright & Wright, Inc. **199**

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ES&T BOOKS

Fine Particles in Gaseous Media. Howard E. Hesketh. x + 214 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1977. \$24, hard cover.

In order to control fine particles, which comprise a serious air pollutant, better knowledge of their behavior is needed. This book presents the latest such knowledge gained from theoretical and experimental data. It explains effects of external forces; behavior in gaseous media; collection methods; size measurement methods; and other related matters. Pertinent "math" and sample problems to test reader comprehension are provided.

Solid Waste Pollution Chart. Roy G. Scarfo, Inc., P.O. Box 217, Thorndale, PA 19372. 1977. \$2.50.

This four-color, 28 x 23 in. chart surveys solid waste sources of all kinds, and lists disposal methods. It shows how wastes pollute lands, and gives composition, lists incineration products, and provides solid waste projections for 1980, 1990, and 2000.

Cases and Materials on Environmental Law, Second Edition, 1973. 1977 Cumulative Supplement. Oscar S. Gray. 620 pages. BNA Books, The Bureau of National Affairs, Inc., 1231 25th St., N.W., Washington, DC 20037. 1977. \$10, paper.

This supplement considers 11 important federal appellate cases decided in 1977, including 2 Supreme Court decisions. Also presented are 13 such cases from 1976, of which 4 reached the U.S. Supreme Court. Legislative developments in water, pesticides, NEPA, and many other environmental sectors are covered. The price is \$25.50 if the parent volume is also ordered.

Future Strategies for Energy Development. ix + 297 pages. Oak Ridge Associated Universities, P.O. Box 117, Oak Ridge, TN 37830. 1977. \$8.25, paper.

Are you pro-nuclear? Anti-nuclear? Is small beautiful, or is bigger better? Advocates of both sides of the nuclear and growth debates took part in a symposium held at Oak Ridge, TN, during the fall of 1976. Here is their debate in print.

American Consulting Engineers Council 1978 Directory. v + 326 pages. American Consulting Engineers Council, 1155 15th St., N.W., Suite 713, Washington, DC 20005. 1977. Members, \$7.50; non-members, \$25, paper.

Some consulting engineers work on hydropower dams; others on skyscrapers; and yet others on water pollution control projects, to name a few activities. Here is a state-by-state list of these engineers, which tells who does what.

Pollution Evaluation: The Quantitative Aspects. William F. Pickering. 208 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016. 1977. \$16.50, hard cover.

Even if the amount of air or water pollution were known exactly, from the numerical point of view, what would the social relevance be? This volume bridges the gap between these social considerations and analytical principles. Analytical techniques are also discussed in great depth. This book is Volume 2 of the Environmental Science and Technology Series.

A Change in the Weather. Fitzhugh Green. 248 pages. W. W. Norton & Co., Inc., 500 Fifth Ave., New York, NY 10036. 1977. \$9.95, hard cover.

Some of civilization's activities make material contributions to upset the biosphere; others may, by contrast, be of help. The author explains what many of these positive and negative effects are now, and could be in the future; and proposes means to combat unintended ecocide. He is the former associate administrator of the U.S. EPA for international activities.

Ecology Field Glossary: A Naturalist's Vocabulary. Walter H. Lewis. xi + 152 pages. Greenwood Press, 51 Riverside Ave., Westport, CT 06880. 1977. \$15, hard cover.

This book presents a working vocabulary from all of the environmental sciences. Meanings and relevances are given, and related terms and concepts are easily located. Tables of measurements, equivalents, and conversions are included.

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ES&T MEETINGS

February 20-22 Miami Beach, Fla.

Fifth Ocean Thermal Energy Conversion (OTEC) Conference. University of Miami/Clean Energy Research Institute

Write: Clean Energy Research Institute, School of Engineering & Environmental Design, University of Miami, P.O. Box 248294, Coral Gables, Fla. 33124

February 22-24 Washington, D.C.
Second Environmental Industry Conference on New Initiatives in Environment and Energy. The Environmental Industry Council

Write: Environmental Industry Council, 1825 K St., N.W., Suite 210, Washington, D.C. 20006

February 23 Atlanta, Ga.
Clean Air Act Forum: Implementation of the Clean Air Act Amendments of 1977. U.S. EPA and the Air Pollution Control Association.

Write: Clean Air Act Forum, Air Pollution Control Association, P.O. Box 2861, Pittsburgh, Pa. 15230

February 23-24 Washington, D.C.
1978 International Conference: Energy Conservation—Comparative Law and Policy. District of Columbia Bar, Dept. of Energy and American Society of International Law

Write: Jane Ottenberg, conference director, District of Columbia Bar, 1426 H St., N.W., Suite 840, Washington, D.C. 20005

February 27-March 1 Washington, D.C.

5th Energy Technology Conference & Exposition. EPR1, American Gas Association and the Dept. of Energy

Write: 5th Energy Technology Conference & Exposition, 4733 Bethesda Ave., N.W., Washington, D.C. 20014

March 1-3 Williamsburg, Va.
National Conference on the Establishment of Standards of Performance for Environmental Laboratories. American Public Health Association

Write: Mrs. Seiko Baba Brodbeck, Environmental Laboratories Conference, American Public Health Association, 1015 18th St., N.W., Washington, D.C. 20036

March 5-8 Chicago, Ill.
1978 TAPPI Annual Meeting and Exhibit. Technical Association of the Pulp and Paper Industry (TAPPI)

Environmental topics will be discussed.
Write: W. H. Gross, TAPPI, One Dunwoody Park, Atlanta, Ga. 30338

March 5-9 Tucson, Ariz.
Waste Management '78. University of Arizona

Write: The University of Arizona, College of Engineering, Special Professional Education, Engineering Building Room 221, Tucson, Ariz. 85721

March 5-10 Southern Pines, N.C.
Stack Sampling for Source Evaluation. The Engineering Foundation

Write: Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

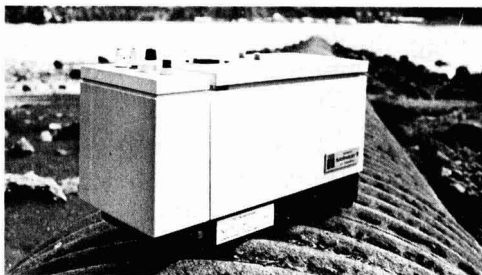
March 6-8 San Antonio, Tex.
4th Annual Symposium on Disposal of Hazardous Wastes. Southwest Research Institute and the U.S. EPA

Write: David W. Shultz, symposium coordinator, Southwest Research Institute, P.O. Drawer 28510, San Antonio, Tex. 78284

March 7-8 Madison, Wis.
Water Storage Facilities. University of Wisconsin-Madison

Write: c. Allen Wortley, Dept. of Engineering, University of Wisconsin-Madison, 432 N. Lake St., Madison, Wis. 53706

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March 10-12 Washington, D.C.
National Conference on Solar Energy. Charles B. Slack, Inc. Meeting Management
Write: Sam Slack or Sal Pacetta, Charles B. Slack, Inc. Meeting Management, 6900 Grove Rd., Thorofare, N.J. 08086

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MARKETPLACE '78 in conjunction with the National Association of Recycling Industries' 65th Annual Convention. National Association of Recycling Industries (NARI)
Write: Jerome Scharf, NARI, 330 Madison Ave., New York, N.Y. 10017

March 12-13 Louisville, Ky.
Seventh Environmental Engineering and Science Conference. University of Louisville
Write: Mrs. Patricia Bell, director, Professional Education, Speed Scientific School, University of Louisville, Louisville, Ky. 40208

March 12-17 Anaheim, Calif.
175th ACS National Meeting. American Chemical Society
Write: A. T. Winstead, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

March 14-16 San Francisco, Calif.
Coastal Zone '78: A National Symposium on the Technical, Environmental and Socioeconomic Aspects of Coastal Zone Planning and Management. National Oceanic and Atmospheric Administration's (NOAA) Office of Coastal Zone Management and others
Write: J. Robert Edmisten, executive director, Coastal Zone '78, P.O. Box 26062, San Francisco, Calif. 94126

March 28-29 Washington, D.C.
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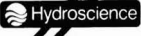
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February 27-March 3 Pasadena, Calif.

Recognition, Evaluation & Control of Occupational Hazards, Course No. 549. National Institute for Occupation Safety & Health and Wichita State University

Fee: \$350. *Write:* Wichita State University, CHCM, Box 37, Wichita, Kans. 67208

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Digital Image Processing of Earth Observation Sensor Data, Course No. 307. George Washington University

Fee: \$495. *Write:* Director, Continuing Engineering Education Program, George Washington University, Washington, D.C. 20052

Call for Papers

March 1 deadline

Surface Mining and Fish/Wildlife Needs in Eastern United States. Eastern Energy and Land Use Group of the Fish and Wildlife Service and West Virginia University

Conference will be held December 3-6, 1978, at Morgantown, W.Va. *Write:* David Samuel, Division of Forestry, West Virginia University, Morgantown, W.Va. 26506

March 1 deadline

Disposal of Oil and Related Materials and Debris Resulting from a Spill Cleanup Operation. American Society for Testing and Materials Committee F-20 on Spill Control Systems

Conference will be held October 8-13, 1978, at New Orleans, La. *Write:* Sam W. Bowman, American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103

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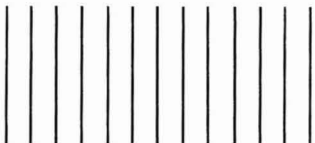
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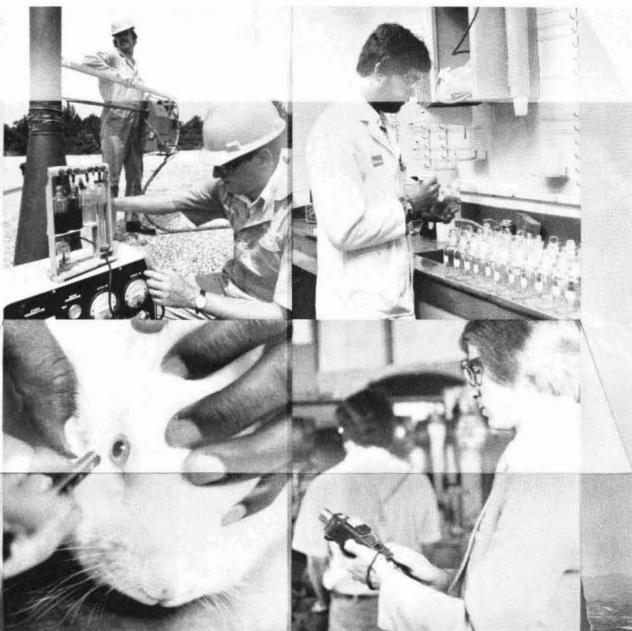
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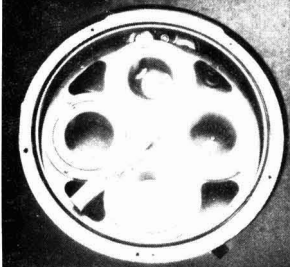


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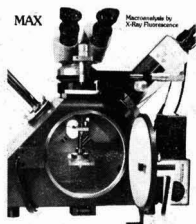
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