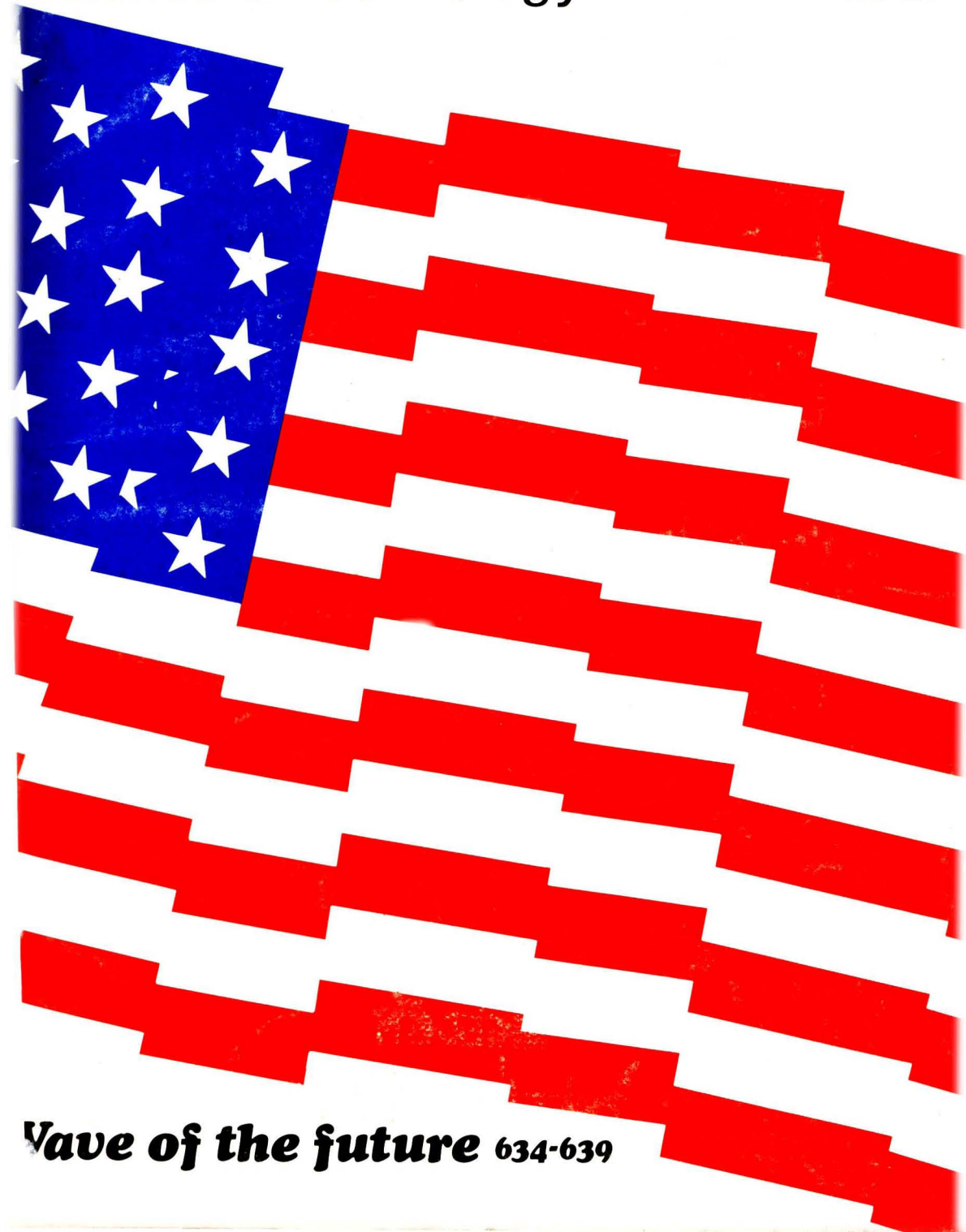


# Environmental

Science & Technology

JULY 1976



***Wave of the future*** 634-639



Designed for indoor or outdoor use, these precision instruments sample gases in ambient air . . . accurately

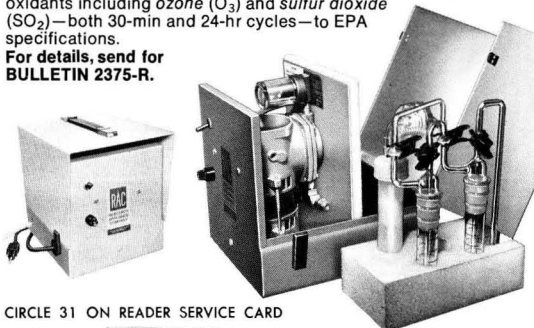
# RAC Gas Samplers

RAC wet-chemical instruments can sample any gas for which accepted sampling/analyzing procedures have been developed. Each design offers specific features that adapt it to a range of sampling operations.

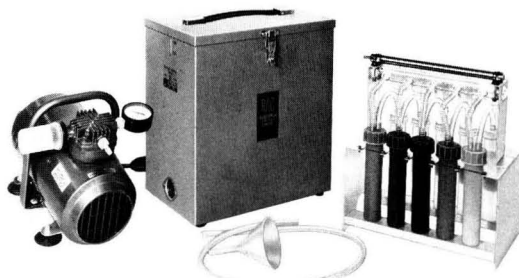
## RAC AMBIENT AIR SAMPLER

This single-gas system uses modular, interchangeable bubbler trains to collect *acrolein* (C<sub>3</sub>H<sub>4</sub>O) and *aliphatic aldehydes* (CHO) to HEW specifications as well as *nitrogen dioxide* (NO<sub>2</sub>), oxidants including *ozone* (O<sub>3</sub>) and *sulfur dioxide* (SO<sub>2</sub>)—both 30-min and 24-hr cycles—to EPA specifications.

For details, send for BULLETIN 2375-R.



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## RAC 5-GAS SAMPLER

This portable bubbler system collects up to 5 different gases simultaneously in one sampling cycle. Furnished in indoor and outdoor configurations, it meets EPA specs for sampling NO<sub>2</sub> and SO<sub>2</sub>. To ensure SO<sub>2</sub> sampling accuracy, an optional thermoelectric cooling/heating system is available. This device maintains the temperature of the SO<sub>2</sub> reagent between 47° and 57°F, thereby providing optimum sample stability. The RAC 5-Gas system also is widely used for collecting ammonia (NH<sub>3</sub>), hydrogen sulfide (H<sub>2</sub>S), CHO and other gases.

For details, send for BULLETIN 2333.

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## RAC PV SEQUENTIAL SAMPLER

This automatic timer-controlled instrument collects 12 consecutive samples of ambient gases over time periods ranging up to 12 days. Individual sampling cycles can range from 30 mins to 23¾ hrs in length. It samples *carbon monoxide* (CO) as well as H<sub>2</sub>S, NH<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub> and other gases.

For details, send for BULLETIN 2340-A.

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## RAC PERSONAL SAMPLER

Suitable for underground, indoor and outdoor sampling, this battery-powered minisampler is NIOSH and MESA approved for collecting respirable particles from the wearer's breathing zone. For sampling *vinyl chloride* and other organic vapors, RAC offers a new sampling head that utilizes charcoal tubes and features an integral flowmeter and flow adjusting valve. This organic vapor accessory also can be used with other existing personal particulate or gas samplers. For details, send for BULLETIN 2392-A.

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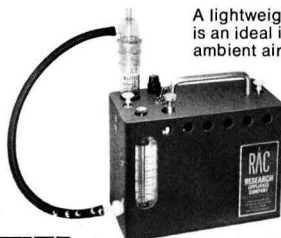


## RAC MIDGET SAMPLER

A lightweight dual-purpose design, this is an ideal instrument for spot checking ambient air to comply with OSHA

requirements. It can sample airborne particulate matter in addition to CHO, H<sub>2</sub>S, NH<sub>3</sub> and NO<sub>2</sub>. An optional battery-powered model also is available. For details, send for BULLETIN 2312AB-R.

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Environmental Instruments / Laboratory Products

# Environmental

## Science & Technology

Volume 10, Number 7, July 1976

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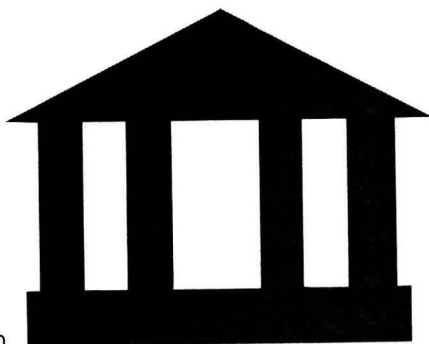
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16 JUL 25 1976

Volume 10, Number 7, July 1976 621



# CURRENT RESEARCH

## Evaluation of candidate solids for high-temperature desulfurization of low-Btu gases 659

P. R. Westmoreland and D. P. Harrison\*

Thermodynamic screening of 28 solids for their high-temperature desulfurization potential used the free energy minimization method. Eleven solids showed thermodynamic feasibility for desulfurization of low-Btu gases.

## Cadmium accrual in combined wastewater treatment-aquaculture system 662

W. B. Kerfoot\* and S. A. Jacobs

Trace amounts of Cd were added to a tertiary treatment-aquaculture system. Cd uptake in two types of phytoplankton and two species of shellfish was studied. Concentrations in the algae increased rapidly until equilibrium was reached, while exposed shellfish showed continuous accumulation.

## Thermal decomposition of manganese sulfate pellets 668

P. R. Mulik, Kun Li\*, and R. R. Rothfus

Finely ground pellets of  $MnSO_4$  were decomposed in  $N_2$  at 805–905 °C. The oxide product was  $Mn_3O_4$ . A topochemical mass transfer model predicts the decomposition rate and indicates that generation of  $SO_2$  at 950–1000 °C is sufficient for sulfuric acid production.

## Kinetic study of HONO formation and decay reactions in gaseous mixtures of HONO, NO, $NO_2$ , $H_2O$ , and $N_2$ 674

W. H. Chan, R. J. Nordstrom, J. G. Calvert\*, and J. H. Shaw

Formation and decay reactions of HONO were studied with continuous FT-IR monitoring of reactants and products. Results indicate that these reactions are a negligible source or sink of HONO at normal NO and  $NO_2$  levels. Reaction rates are presented.

## Multielement and chlorinated hydrocarbon analysis of municipal sewage sludges of American cities 683

A. K. Furr, A. W. Lawrence, S. S. C. Tong, M. C. Grandolfo, R. A. Hofstader, C. A. Bache, W. H. Gutenmann, and D. J. Lisk\*

Analysis of sewage sludges from 16 American cities was done for 68 elements, dieldrin and PCB's. High concentrations of certain toxic elements were found in sludges from some cities.

## Industrial waste disposal. Excess sulfuric acid neutralization with copper smelter slag 687

L. G. Twidwell\*, J-R. Hwang, and R. E. Dufresne

A leach lime roast process for extraction of Cu and Zn from copper reverberatory slag with waste  $H_2SO_4$  has been developed. Eighty-five percent of the Cu and Zn can be extracted; 90% of the sulfur is retained.

## Reactivity scale for atmospheric hydrocarbons based on reaction with hydroxyl radical 692

K. R. Darnall, A. C. Lloyd, A. M. Winer, and J. N. Pitts, Jr.\*

A five-class scale is developed based on rate of removal of hydrocarbons and oxygenates by reaction with OH. Unlike others, this scale focuses directly on the initial photooxidation rates. Additional hydrocarbons can be added, once their rate of reaction with OH is known.

## Chemical dynamics of a polluted watershed, the Merrimack River in Northern New England 697

J. Caesar, R. Collier, J. Edmond, F. Frey, G. Matisoff, A. Ng, and R. Stallard\*

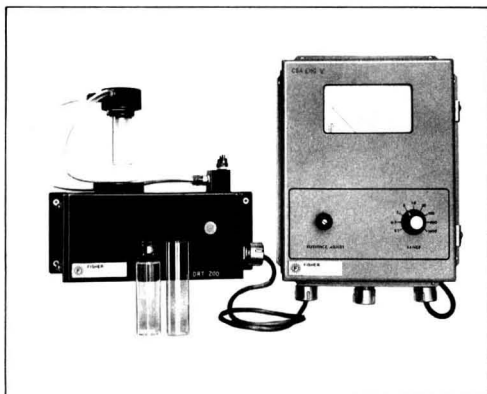
Major ion and nutrient composition of the Merrimack River was monitored for one year. Concentration dependence of these elements on flow was modeled using two input components. One has a constant mean composition and steady flux, the other has a composition which is flow dependent.

Credits: 630 (center), UPI; 634, 635, ES&T's Julian Josephson; 637 (top), J. L. Proffitt; 637 (bottom), Photo Optik's Barry Barron; 638 (center and right), Dept. of Transportation; 640, National Bureau of Standards; 642, National Coal Assoc.; 643, ES&T's Julian Josephson

Cover: Norman Favin and Diane Reich

\* To whom correspondence should be addressed.

# Is the '77 Clean Drinking Water Act a tough act to follow?



Not for the Fisher DRT-200 Turbidimeter with flow-through cell for continuous monitoring plus exceptional sensitivity for measuring turbidity down to very low levels.

Looking ahead to the '77 requirements and their more demanding turbidity measurements, from ultra-clear to highly turbid samples, DRT-200 measures up\*. First of all, it meets the Formazin verification requirement of the Environmental Protection Agency for in-line monitoring (lets you verify with a primary reference standard or Formazin solution without stopping flow). And, DRT-200 can also measure your laboratory grab samples at the same time it's monitoring on-stream, without stopping flow. Now, one DRT-200 can do the work of two instruments and save you money.

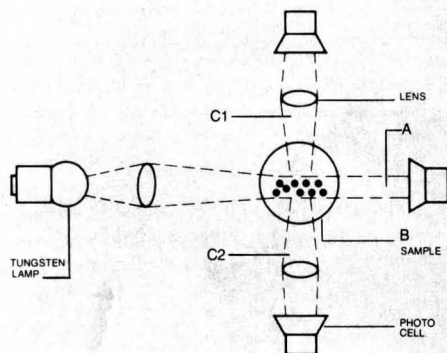
\*International standard unit for measuring turbidity in water treatment is the Nephelometric (NTU), Formazin (FTU) or Jackson (JTU) Turbidity Units. These unit terms are directly interchangeable.

## Truth and Turbidity

Experts agree — accurate turbidity measurements depend upon linearity. True 90° Nephelometry and three photocell detectors make the DRT-200 the linearity leader (see drawing).

This strict linearity enables switching from range to range without recalibrating. Even samples over 40 NTU do not require recalibration. DRT-200 offers nine sensitivity ranges from 0.1 to 1000 NTU full-scale deflection (sensitive to 0.002 NTU change).

*Fisher Turbidimeters measure turbidity by comparing the direct light (A) passing through a sample (B) with the amount of scattered light measured at 90° to left (C1) and right (C2) of the light path. The output signals produced are linear with changes in turbidity (Formazin values).*



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# Don't calibrate. Rotate!

Gilson constant-pressure volume-compensated differential respirometer allows you to complete an experiment in the former set-up time.

Digital readout in numbers of microliters

**For manometric respirometry studies — plant tissue, animal tissue, and micro-organism oxygen uptake; mitochondria activity; photosynthesis, enzyme activity, and B.O.D.**

A calibrated micrometer returns the manometer fluid to its balanced position by movement of a piston in the enclosed volume. This obviates the need for calibration of glassware and simplifies calculations.

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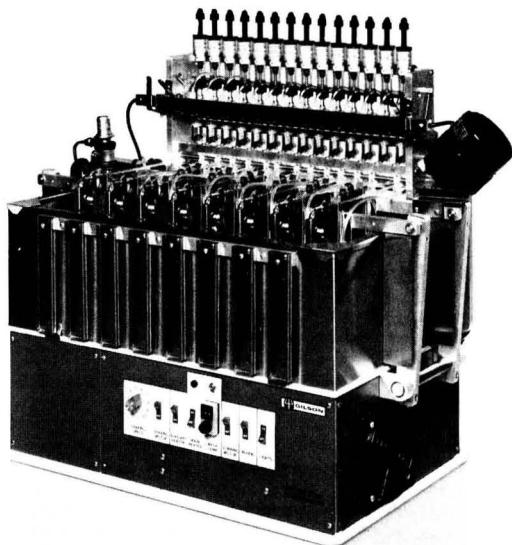
Standard models connect the active flask and reference chamber to stationary volumeters by means of capillary Tygon®\* tubing. (Not applicable for use with gases which pass through Tygon.)

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# Gilson Respirometers

CIRCLE 4 ON READER SERVICE CARD

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1976 issue, page 553, or write Katherine I. Biggs,  
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## Universities and social relevance

The environmental issue has provided an excellent demonstration of the problems facing American universities. Critics of traditional university programs have argued strongly for increased "relevance" in curricula, stronger ties of funding to job market demands, and even for extra-university control of the directions of scholarly research. The recurring theme in such criticism revolves around the assumption that universities have an institutional responsibility to function as a social problem solver.

It is very much to the credit of universities that they have staunchly resisted this notion. The pressures of the early Seventies for the undergraduate production of environmental generalists have largely dissipated with the realization that "relevant" environmental preparation is best served by disciplinary depth coupled with an opportunity for advanced study. At the graduate level the various professional programs of universities have been particularly responsive to environmental demands with more than 4000 M.S. graduates in the engineering and public health fields since 1962. They have been particularly relevant to social need—bridging the transient demands of professional job markets with fundamental knowledge.

Disciplinary and professional strengths are the principal means through which universities contribute to society, the universities serving uniquely as collectors and examiners of truth and guardians of cultural heritage. To remain active in this role, university personnel must be continuously involved in research and the examination of basic ideas constituting the disciplinary substance. The advances of the last few decades in agriculture, medical science, engineering, and the natural sciences are a convincing testimony to the ultimate social reward for the subsidy of research and graduate education. Universities are not primarily problem-solving institutions, and no quicker way could be found to destroy their real value than to immerse them in short-term social missions.





# Philips SO<sub>2</sub> monitors: 90 days, 90%... 90 years?



**1969**

The first Philips SO<sub>2</sub> monitor is installed in the U.S.



**1976**

... over 60,000 data hours later this Philips SO<sub>2</sub> monitor is still on duty, still producing 90-95% valid data on an annual basis.

This is why...

## Philips designed the monitor around a 90 day scheduled maintenance program

90 day unattended operation, together with 90 day scheduled maintenance establishes the basis for Philips unequalled field performance and for its broad acceptance. Implied by these tough field performance criteria are design standards of the highest level. Today, seven years after the introduction of the PW9700 SO<sub>2</sub> monitor, Philips remains the *only* manufacturer to offer 90 day standards for unattended operation and for scheduled maintenance—no one else is even close.

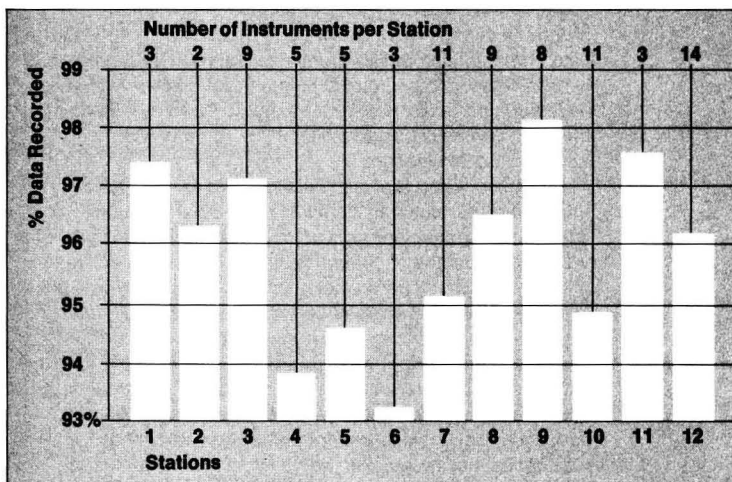
Design criteria that make the 90 day scheduled maintenance program possible include...

Highest quality components. Components selected for the monitor must pass a quality assurance program to satisfy the necessary MTBF for 90 day unattended operation. Success of this program is attested by the more than 2500 monitors now in the field worldwide and routinely reporting a 90% or better data recovery.

Automatic regeneration of reagent. A constant level coulometric cell with automatic regeneration of reagent provides for a 6 month life of the electrolyte.

## Philips designed the monitor around a built-in data quality program

Continuous data validation. Automatic, daily systems zero\* and dynamic span† checks are made



**High quality means high performance:** 95.9% average recovered data from a 12 station 83 monitor system. Record covers a 10 month period. The data above was validated by a multi-point external calibration using the following schedule: 24 hours, 7 days, 45 days.

\* An activated charcoal filter incorporated in the monitor provides a pure air sample to generate a system zero signal.

† In the PW9755 a thermostatted SO<sub>2</sub> permeation source, traceable to an NBS standard, is used to provide a known amount of SO<sub>2</sub> when a calibration command is received.

to assure continuously validated information from the monitor.

### **Philips monitors get off to a good start**

The Philips monitor is installed and made operational at the customer's facility by a Philips service engineer. The instrument is released to the customer only after the system has been verified as meeting specifications. This service is provided to the customer as part of the purchase price.

### **Philips nationwide service organization assures prompt local support**

Our 12 month field warranty brings prompt on-site service to the customer as required . . . and at no cost to the customer.

Philips highly trained service engineers operate from 14 service offices throughout the nation. On-going schooling programs for these engineers assure up to the minute competence in their performance.

### **Philips support assures continuing performance**

At the time the equivalency document was published, our PW9700 SO<sub>2</sub> monitor had been superseded by the PW9755 (see below) and was no longer in production . . . Philips, nevertheless, embarked on a program, prior to the promulgation of the document, to bring the PW9700 in line with future requirements, and filed for equivalency on behalf of this instrument.

### **Philips listens to its customers**

After extensive field experience and component design improvement programs, Philips, in 1976, introduced an updated version of the PW9700, the PW9755—even though the older model still has no peer for field performance.



# 1981

Philips has every reason to believe that its first U.S. monitor will be operationally effective in 1981, the year in which all monitors must be EPA equivalent. This is why equivalency for our 1969 model was important: we wanted those many companies and institutions who had purchased the PW9700 to be able to achieve the use that was originally built into this instrument . . . and this is why our present customers can be confident that in 1981 they will still be achieving 90-95% valid data on an annual basis.



# 2059?

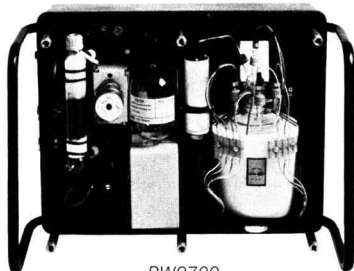
Still in use? Probably not. But as the first 90 day monitor for the control of ambient air quality, the PW9700 will have long since earned its place in history.

**1976** Valid year to purchase your first (or 90th) Philips SO<sub>2</sub> monitor. Call us today (914-664-4500) and ask for the EQP Group (Environmental Quality Products). They'll be glad to get things moving for you.

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PW9755



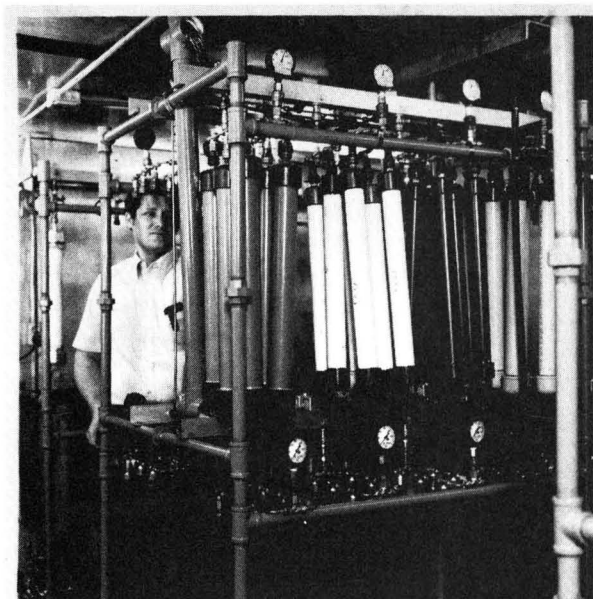
PW9700



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And so does the manufacturer. He *pays* us for our services and, in effect, he is paying us to find anything that may be wrong.

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When purchasing plastic pipe, joints, fittings and related materials, specify NSF. Health officials do.

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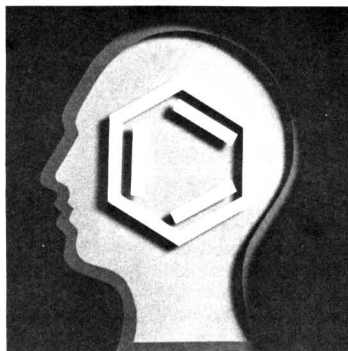
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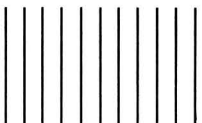
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# CURRENTS

## INTERNATIONAL

**Hungary has passed a new environmental protection law** that provides a framework for enforcement of antipollution decrees. The law covers the entire environment rather than just one or another sector. About \$1 billion will be allocated for environment in that country, according to József Böndör, Hungarian Minister of Construction and Urban Development. **Meanwhile, Sweden has proposed a Work Environment Act** aimed at solving problems of safety and health hazards. The Swedish Work Environment Commission calls for updating hygienic standards, increased enforcement powers, environmental planning, and fulfillment of social and psychological needs in the workplace.

**Walter Marshall, deputy chairman of the U.K.'s Atomic Energy Authority,** sees no acceptable future for the United Kingdom without the simultaneous development of advanced techniques for enhanced coal utilization, energy conservation strategies, and nuclear power. Speaking at an international symposium on electricity R&D planning, Marshall stressed his concern for the U.K.'s stance of complacency in the face of an energy glut in the decade 1980-90 when the North Sea oil will make the U.K. self-sufficient. The U.K., Marshall says, has also been examining solar, wind, wave and geothermal power, and finds the use of wave power to produce electricity the most promising technology. However, the U.K.'s prospects for solar power are not negligible.

## WASHINGTON

**In its 1975 annual reports to Congress, the EPA reported** improvements in air quality and gains in water pollution control. Average year-around levels for SO<sub>2</sub> declined by 32% while particulate matter decreased by 17%. Of the 20 000 major stationary sources of pollution, 82% now met emission limits or are meeting compliance schedules. Improvements in carbon monoxide levels were recorded in urban areas of Calif., N.J., N.Y., and Washington, D.C. In the first reports the states have prepared assessing their water quality, the trend was toward improvement of

conditions. Waterways cited for improvement were Lake Erie, Detroit River, and San Diego Bay. Also, concentrations of pesticides in tissues of fish have declined.

**EPA administrator Russell Train reported that the economic effects of environmental regulations** on the petroleum refining and electric utility industries are reasonable when capital availability, consumer product prices and employment impact are considered. For the period 1974-83, the petroleum refining industry will have to make capital investments of about \$5.9 billion to comply with environmental regulations, about 25% of their total capital expenditures for the period. At the consumer level this



EPA administrator Train

translates to an increase of 1¢/gal, or a 2% increase by 1983. About 13 000 jobs are expected to be created. For the electric power industry, in the period 1975-85, capital expenditures are estimated at \$25 billion for compliance, or about 10.5% of the total projected capital outlays. Average monthly electric bills in 1985 will be about 6.6% higher than an average bill of \$42.40/month. Employment impact is expected to be minimal.

**The Supreme Court will review EPA's authority to force states to adopt transportation plans** under the Clean Air Act. Several lower courts have issued conflicting rulings on this matter. Specifically, the Court will review the issue in cases from Calif., Ariz., Md., Va., and Washington, D.C. The Supreme Court is still deciding whether to review the U.S. Appeals Court for D.C.'s ruling that EPA has the authority to require a phasing out of lead in gasoline. The Supreme Court's decision in this matter is expected before it recesses, sometime this month.

**Under the National Water Data Storage and Retrieval System** the U.S. Geological Survey can supply data on more than 150 million streamflow, water-quality and groundwater measurements collected at more than 100 000 sites throughout the U.S.

**The Federal Power Commission has authorized an interstate pipeline** to supplement its natural gas supplies with synthetic (methane) gas made from cow dung. The volume of gas covered by the order is only 820 million cubic feet a year, less than 1% of Natural Gas Pipeline Company's annual purchases. Still this is a significant step toward the use of biomass conversion as an alternative source of energy.

**Capital expenditures for pollution abatement in 1975 increased 17%** from \$5.6 billion in 1974 to \$6.5 billion in 1975, according to a recent Dept. of Commerce survey. This increase in pollution abatement spending by nonfarm business accounted for 60% of the \$1.6 billion increase in 1975 total new plant and equipment spending reported in the survey. Antipollution expenditures are anticipated to increase by 12% in 1976.

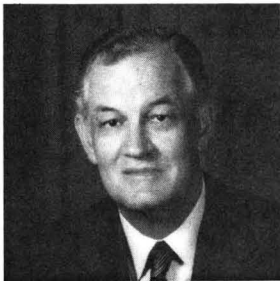
**Under a new SEC amendment, public corporations must disclose material capital outlays for environmental control facilities** in their proxy statements, annual reports and other statements to shareholders. The Securities and Exchange Commission withdrew a second proposal, out for comment since last October (see *ES&T*, December 1975, p 1105), that would have required companies to provide limited information about environmental standards that they were not in compliance with.

## STATES

**Construction problems on the Trans-Alaskan Pipeline have surfaced.** In its own audit of the quality of welds on the 48-in. wide pipe, Alyeska, the consortium building the pipeline, found some 28 cracked welds out of 1700 welds already made on pipe in place. No defective welds occurred on pipe buried at river crossings, but radiographs of these welds were missing. The minimum cost for repairing the cracked welds was

estimated at \$5–10 million. The Dept. of the Interior has ordered an independent audit of the audit that could delay the targeted mid-1977 completion date and result in millions of dollars of repair work. Other deficiencies were found at elevated big game crossings where 116 out of 211 built to date were less than the specified minimum clearance of 10 ft.

**Sale of pull tab cans at retail outlets is banned in Virginia after January 1, 1979.** Legislation to establish a litter control program was also signed into law by Governor Mills E. Godwin, Jr. The Dept. of Conservation and Economic Development is to conduct a program to control, prevent and eliminate litter, while the Dept. of



Virginia governor Godwin

Highways and Transportation is to survey the state for types of litter discarded and report its findings by November 13. Under the law, an annual litter tax of \$2.50 is to be levied against every manufacturer, wholesaler, distributor or retailer of foods, groceries, tobacco products, soft drinks, beer and wine, newspapers, cleaning agents and other products.

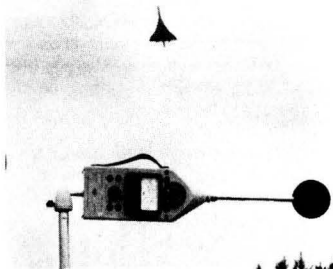
**Maryland officials challenged the U.S. EPA's contention** that the Dickerson sewage treatment plant would be too expensive and present health hazards. Prince Georges and Montgomery counties, the Washington Suburban Sanitary Commission and the state concluded that building Dickerson would be \$31 million cheaper than the alternative proposed by EPA, which was an expansion of the Piscataway facilities in Prince Georges County. In their response, the Maryland officials claimed that construction of Dickerson could be completed by 1981 should construction begin now, while expansion of the Piscataway facilities would take until 1985. Rather than present a health hazard, the Maryland report said that a Dickerson plant would recharge the Potomac River with high-quality water above the drinking water intakes, and supplement the water supply in dry years. EPA's response is expected this month.

**The Vermont Whey Pollution Abatement Authority sold \$9.6 million of bonds** recently to finance facilities to dry the whey, a by-product of cheese production, to a protein-rich ingredient in various food products. The bonds, rated A-1 by Moody's, were priced to yield between 4.6% in 1978 and 7.25% in 2006. In Wisconsin 400 small cheese plants are disposing of whey by spreading it on meadow and corn plots. During the 3-yr experimental period, crop yields have increased. Guidelines on methods of spreading whey without producing pollution problems are available from Professors A. E. Peterson and R. D. Powell of the University of Wisconsin.

**The California Air Resources Board issued 218 pollution violation notices against seven large oil refineries.** Companies cited by the Board were Standard Oil for 82 violations, Shell for 32, Atlantic-Richfield for 34, Union for 27, Mobil for 20, Gulf for 21 and Texaco for 2. These notices, the first ever issued, cited the companies for permitting smog-producing vapors to escape from their petroleum storage tanks. Several of these southern California companies have improved their facilities; violation notices will be cancelled against those companies who repair their oil storage tanks to comply with the law.

## MONITORING

**The FAA has begun a \$1.2 million monitoring program including noise**, to assess the impact of Anglo-French Concorde supersonic flights into and out of Dulles International Airport in Fairfax County, Va. The program is monitoring *all* flights into and out of the airport for emissions, sonic booms, noise levels and community response. The monitoring period is for 12 months



Checking Concorde noise

with 4 months of analyses, but the Federal Aviation Administration will probably monitor for the full 16 months of the Concorde's trial run. Eight permanent monitoring sites have been established to collect data 24 h/day; in addition, 5 portable units are available

for monitoring at up to 23 different sites. A full report of the FAA's findings will be available on the 10th day of every month. Fairfax County has established its own monitoring program.

## TECHNOLOGY

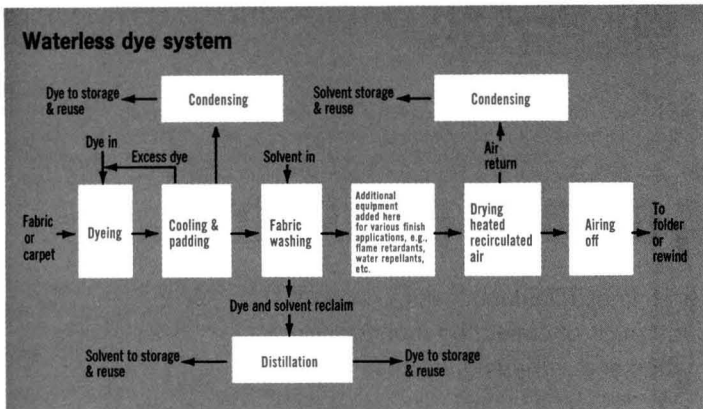
**A chemical process for fracturing coal to remove pyritic sulfur** "compares favorably with current preparation techniques," according to Syracuse Research Corp. (SURC, Syracuse, N.Y.). The process involves comminuting agents; at present, anhydrous and hydrous liquid and gaseous ammonia, 99% of which can be recovered for reuse. Ammonia is able to fracture the coal along natural faults without affecting the coal's physical and chemical properties, and only slightly increasing the nitrogen content. SURC expects that many eastern coals could meet federal clean air regulations through this comminution process, while the cost increase would be "very modest."

**Converting NO<sub>x</sub> in tail gases to commercially marketable nitric acid (HNO<sub>3</sub>)** is done by the CDL/VITOK process of Chenoweth Development Laboratories, Inc., and VITOK Engineers, Inc. (Louisville, Ky.). The process involves scrubbing with HNO<sub>3</sub>, which reduces NO<sub>x</sub> to the desired level; it will be used on a 350-tpd HNO<sub>3</sub> plant now under construction.

**Municipal waste-water treatment processes are helped by sodium bicarbonate.** The chemical aids both aerobic and anaerobic digestion, according to the main U.S. producer of the chemical, Church & Dwight Co. (Piscataway, N.J.). In anaerobic systems, two bacterial processes—acid formers and methane formers—compete, resulting in poor microbiological digestion. At the Hightstown, N.J. plant, the addition of NaHCO<sub>3</sub> tripled methane production, providing all the fuel for the plant. The chemical also increases the rate of biodegradation. A 5% increase in biodegradation translates to an increased plant capacity of 5%. For example, normal digester turnover of 20 days is reduced to 19. Alternatively a 60 mgd plant is upgraded to 63 mgd.

**Textile dyeing with no water, 50% less energy, and 60% less capital cost for new facilities?** According to Martin Processing, Inc. (Martinsville, Va.), all this is possible because of a process that uses organic solvents kept in a closed system. In this continuous process, the solvents are always being purified and recycled. The machinery takes up less than 20% of floor space





needed by water-based processes. No dyestuff is lost, and complete color changes are achievable in 4–5 min. Also, the solvent system allows flame retardants to penetrate the dyed fibers fully, not just to the surface, as do water-based methods. The elimination of water cuts investment and energy needs also because wastewater treatment equipment is unneeded, since there is no effluent.

**Simultaneous removal of stack gas hydrogen chloride (HCl), hydrogen fluoride (HF), and SO<sub>2</sub>**, with efficiencies of more than 90%, is accomplished by use of the Holter process. This process, developed by Saarberg-Holter Umwelttechnik GmbH (Saarbrücken, W. Ger.), is presently in use for SO<sub>2</sub> removal at the Weiher Power Station II of Saarbergwerke AG, and has logged 7000 h of operation. Stack gas temperature is lowered and the gas is "washed" with a special fluid. After further venturi washing, drying, separation, and treatment, a high-quality gypsum results. The process, which uses no lime suspension, but rather chloride ions and "Absorben 75", recycles all washing water. The prototype plant handles up to about 80 000 scfm.

**How do you get rid of unwanted TNT without having a blast?** To satisfy EPA requirements, the U.S. Army Picatinny Arsenal (Dover, N.J.) is answering that question by mixing TNT, a 10% ratio, with organic matter such as grass clippings, leaves, and garbage under controlled conditions of moisture and aeration. Rich in nitrogen, the mixture attains a temperature of 160 °F after bacterial action starts, and becomes fertilizer in a few days. When mixed with phosphorus-containing nutrients, the resultant fertilizer can be useful for vegetables, as well as shrubs and lawns. Another Army technique of explosive disposal uses fluidized-bed combustion in a water slurry with a

catalyst at over 1600 °F on a bed of pelletized alumina; detonation cannot occur, and polluting exhausts are reduced.

## INDUSTRY

**Douglas Barno, Owens-Corning Fiberglas Corp.'s manager**, market development, corrosion-resistant materials, told a Society of the Plastics Industry meeting that the water and wastewater treatment market has been identified as a target market for Fiberglas Reinforced Plastics (FRP). He predicted that high capital spending by municipalities and industry for the construction of water and wastewater treatment plants will cause FRP sales potential to increase over the next 5 yrs. Barno said that by 1979, such products as the FRP-belled clay pipe joining system for vitrified sewer pipe, and other related items will spur a total FRP market growth for the water and wastewater sectors of 44% by 1980.

**Calgon Corp. has introduced a new granular carbon adsorption service** for control of dissolved organic materials, including those that cause taste and odor problems in public potable water systems. The modular carbon system can be for final treatment after sand filtration, or it can provide simultaneous filtration and absorption of settled water. Virgin carbon would be used for initial fill and as used carbon replacement, according to T. A. McConomy, director, Calgon, Adsorption Systems. McConomy said that the service, a first in the water treatment industry, makes granular carbon adsorption available to smaller plants needing effective and economical organics removal from drinking water. The user would pay a monthly fee for the service.

**Joseph Schapiro, president of the Institute of Scrap Iron and Steel, Inc. (ISIS)**, Washington, D.C., said that

market distortions are the biggest barrier to recycling. He noted that while purchases of iron and steel scrap in 1975 (37.1 million net tons) were 28% less than in 1974, domestic iron ore production fell only 3%, and imports 2% from a record 53.8 million net tons in 1974. The markets for scrap "just aren't there," Schapiro said, and called on the federal government to address itself more to resource recovery problems. Then, private involvement and investment should increase, he predicted. Schapiro complained that "we dig for more ore while we clutter the countryside with more metallic waste."

**Croll-Reynolds Engineering Co., Inc. (Stamford, Conn.) is supplying** a battery of 3 duplex tubular filter systems that will clarify desalted potable and wash water for the crew of SEMAC-I. SEMAC-I is a unique, semi-submersible pipeline-laying barge—the first to be built in the U.S., by Alabama Dry Dock and Shipbuilding Co. (Mobile)—that will commence operations in the North Sea next year. The filters can remove particles as small as 25 µm from water flowing as fast as 150 gpm, and will provide the barge's crew of 264 water of quality "equal to municipal supplies or better," according to Croll-Reynolds. Downtime and maintenance would be minimized.



Utilities president Dieckamp

**Herman Dieckamp, president of General Public Utilities Corp. (New York, N.Y.)**, told a financial analysts' conference that heat storage will help to reduce investment demand of public utilities as depletion of oil and gas reserves stimulate a shift to electricity for space heating and cooling. "Heat storage involves use of various devices ranging from ceramic storage heaters used in Europe to a simple tank of hot or cold water tied to water or forced-air distribution system," Dieckamp explained. He said that investment needs for new generating capacity would be cut because heat storage help to spread demand over the 24-h day and take pressure off peak demand. A home using 3000 kW/mo could be served with a storage tank 10 ft long and 3 ft in diameter, Dieckamp pointed out.

# Acquiring data on pollutants

E-H Research Labs (Oakland, Calif.) reviews  
the fundamentals of collecting monitoring  
information and retrieving the results

Pollution control has become a major concern of today's society, fostered by increasing levels of population and industry. Before our society can control pollutants, they must first be measured and quantified. Pollution exists in many forms, and methods of measuring pollution are even more numerous. There is, however, one common denominator for all methods—the requirement to collect data about the pollution.

For processing large volumes of data, the digital computer has become the most efficient and desired tool. A necessary first step to such processing is to provide a system for feeding data into the digital computer.

The effectiveness of such a system relies on its capability to accept data from a number of sources. If the data are in analog form, they must be converted to digital form. All the data must then be reformatted into a form compatible with the computer, or a manner suitable for recording on a computer-compatible storage medium such as magnetic or paper tape. In some cases, it is also required to transmit the data over telephone lines to a central collection station.

## Historically

The three basic methods of collecting pollution monitoring samples and retrieving data are:

- The manual method that requires a technician to place collection jars, photosensitive plates, and absorbent filters at selected sites. After the proper exposure to the environment has been attained, the samples from the collection device are gathered and returned to the laboratory for analysis.

- Auto-sampler devices are designed to sample at preset intervals by a timing mechanism, typically a spring-wound clock. The samplers usually operate unattended over a long period, collecting air and water samples in jars, balloons, filter paper, or the like. When the sampling device has been loaded to capacity, it is collected by the technician and returned to the laboratory for analysis.

- The on-line chemical analysis method offers the ultimate in raw data collection. A manifold is often used to draw in a large sample of ambient air or water and, from the manifold, each instrument draws its required volume of sample for analysis.

Along with these historical methods of sampling are associated certain methods of data collection and reduction. Each instrument has some type of detector that generates information that must, in some fashion, be recorded in a form readable by humans, who are the final analytical or decision device.

The strip-chart recorder has played a predominant role in the area of recording devices. Points must be selected by the technicians' eye and values assigned to those points; the values are transcribed to some type of log book or summary. This method of data recording is obviously vulnerable to human error.

Digital-printed tape has been used as an attempt to replace the strip-chart recording. To some degree, this alternative has been successful. However, digital "strip-charts" are difficult to file. The information on the tape is then usually transposed to a log book or summary sheet. Here again, the potential for human error exists.

With these two methods of recording data, there is another associated procedure; the log book or summary sheet is not the final stopping place. For complete analysis, all of the data collected must eventually be processed by a digital computer.

## Data entry

The most widely used method for data entry to a computer is the keyboard of a keypunch or teletype. This introduces still another level for human error—the keyboard operator.

The obvious way to eliminate human error is to by-pass the human handling of data. Recording directly from the analytical instrument to an off-line recording device is one of the most cost-effective approaches. This method allows the re-

coding of raw, digitized data in an attended fashion, and improves the accuracy and reliability of the source data. Raw data, having been stored on a computer-compatible recording medium, is then always available for later and/or repetitive analysis. Off-line recording devices range from the teletypewriter to esoteric high-speed magnetic tape recorders.

The teletypewriter (TTY) is possibly the most versatile tool in its class. The keyboard of the TTY allows the user to annotate the data with his own observations taken between the pre-determined recording intervals. At the other end of the scale, the magnetic tape recorder provides an easily handled bulk storage medium. Magnetic tape also has a speed advantage over the teletype.

A teletypewriter operates at a maximum rate of 10 characters-per-second. To make recordings from 20 instruments, with the data word from each channel containing 8 characters, the maximum speed 20 channels can be recorded is once every 16 seconds. On the other hand, if magnetic tape is used as the recording medium, the recording time can be greatly reduced. Magnetic tape recorders generally operate at 300 characters per second. Using the previous example of 20 channels with 8 characters for each channel, it would be possible to record 20 channels every 0.5 seconds. The point to bear in mind is that the ultimate speed of the system is generally constrained by the speed of the recording device.

## Mini-computer

With the continually decreasing cost of the mini-computer and programmable calculator, there exist certain situations in which an on-line processor system can be justified. In any continuous monitoring application, raw data must eventually be reduced. In reporting out-of-limit conditions and trend data, as well as units, data conversion is usually desired. Small computing devices are ideally suited to these situations.

A min-computer with as little as 2K

words of storage can store high/low values for 100 channels or sensors. Routines stored in the computer can detect out-of-limit conditions and be made to signal (audibly or visually) an operator monitoring the system.

Methods of sample collection, data recording, and data reduction are many and varied. Therefore, in specifying a data acquisition system the user must be wary of buying equipment that will limit the possible approaches to problem solving.

**Configurations**

A data acquisition system must also be able to accept the output of any sensor, transducer, or instrument. The methodology and chemistry of any monitoring application will change; instruments and sensors are constantly becoming more sophisticated. Also, new parameters become of interest to the investigator. Therefore, an AutoRanging analog to digital converter with special circuitry to allow sample rates of up to 50 samples per second is a desirable feature.

In every pollution monitoring configuration there will inevitably be instruments with binary coded decimal (BCD) outputs. Provision should therefore be made for sufficient BCD input of at least two such instruments.

Instruments must also be calibrated on some predetermined schedule to maintain accuracy of data. Calibration requires that

the operator have available some means of reading the output of the instrument at the time of calibration.

Recording data at pre-determined intervals is an historical standard of data collection. Continuous recording of changing air samples has not been proven to be of any value. The SAROAD parameters of the U.S. EPA require the minimum sample to be 1-h average of data collected over that period. Most monitoring agencies are sampling at from 1-5 min intervals to substantiate a 1-h average.

Since no well-defined standard for recording intervals has been adopted, the interval timer of a data acquisition system must be variable over a broad range in small increments. In addition, the timer should have output lines to control external devices such as tape samplers and water dilution devices and periodic calibration checks for certain analyzers.

**What to watch for**

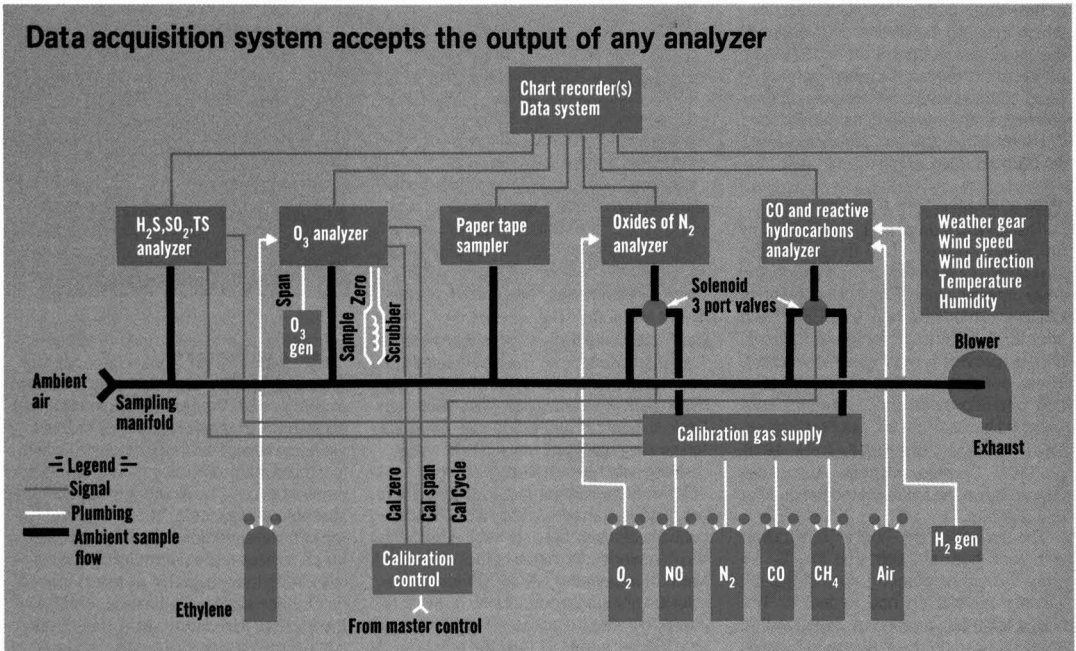
The number of channels the user should order with the initial system can be a crucial decision. Many data acquisition systems are factory built with a specified number of channels and require extensive rewiring to increase capacity.

One of two situations are likely to occur. The user may buy only the number of channels needed to fulfill his present requirement, plus one or two spares. By the time the system is delivered he finds

himself with more instruments than inputs, so costly modifications are required; or a system with full capacity is ordered (somewhere in the area of 100 channels) and only 10 or 20 channels are ever used.

Another very important standard feature of a well-designed system is an output section that has a "slot-configuration." A "slot-configured" system allows the user to change between recording devices by simply inserting one or two printed circuit boards in this system. A data acquisition system is most cost effective where data are recorded on a computer-compatible medium. Because recording devices are so numerous, the investigator ultimately upgrades his recording system as the sophistication of his application changes. Initial cost may dictate he use a currently available 10 character-per-second typewriter. As money becomes available and more instruments and sensors are included in the monitoring station, the investigator will most likely progress to a high-speed paper tape punch, 1/2 inch magnetic tape, and ultimately to his own dedicated mini-computer or calculator.

Present needs seldom reflect future requirements or desires. Ideas may change; requirements and available money may change. To be really useful today, as well as tomorrow, a data acquisition system must be a versatile, flexible tool for the user.





For America's 200th birthday, Concern, Inc.,  
and three federal agencies show how environmental  
and energy goals can be very compatible

# Clean energy for the Bicentennial

Among the objectives of the various American Revolution Bicentennial events is not only the celebration of the past two centuries, but the development of a vision of the century to come. This was the view expressed to *ES&T* by Aileen Train and Nancy Ignatius, chairman of the board and chairman of the executive committee, respectively, of Concern, Inc. (Washington, D.C.), as they described their Bicentennial clean energy exhibit, which officially opened on Washington's Mall in late May.

This exhibit, in which the public can operate many of the components, stresses energy conservation, and solar and solar-related energy technology that is practical and available at this time. It also shows its viewers that the efforts for energy independence, and for maintenance and enhancement of environmental gains need not work at cross-purposes.

The exhibit, which conservatively 1 million people are expected to view before it "goes on the road" in November, was sponsored by ERDA, the FEA, and HUD. It covers about 10 000 ft<sup>2</sup> not far from the U.S. Capitol, and cost approximately \$325 000, all told. Concern, Inc., which initiated the efforts culminating in the exhibit, was chartered in 1970 as a non-profit organization whose aim is to keep citizens informed concerning environmental improvement. Its publications, such as *Eco-Tips*, for example, reach 70 000-75 000 people.

## Where the emphasis is

The exhibit's emphasis, exemplified by an approximately 600-ft<sup>2</sup> house-like structure, is on energy conservation and solar energy, John Bradburne, chief of ERDA's Exhibits Branch, told *ES&T*. The structure's roof is 16 ft high at its apex, and is provided with solar collectors. These collectors, of flat-plate configuration, which provide space heating, were supplied by Solaron, Inc., of Fort Collins, Colo. (George Lof, *ES&T*, April 1976, p 315). Charles Maltbie Associates (Moorestown, N.J.) fabricated the building and exhibits.

The heating of the "house" is by hot air with rock heat storage, and the hot air goes through a plenum, so that exhibit viewers have a chance to feel it. The house itself has sectioned walls, so that the public can be made aware of modern



## The federal agencies involved

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**ERDA** = Energy Research and Development Administration

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**FEA** = Federal Energy Administration

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**HUD** = Department of Housing and Urban Development

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insulation techniques. The exterior is built of energy-conserving materials.

Since solar cooling requires higher temperatures than solar heating, concentrating collectors, provided by Owens-Illinois, are used. The evaporative system associated with the exhibit's cooling system was designed by Wallace Sheet Metal Co. (Gainesville, Ga.), while the 3-ton chiller unit itself is a product of Arkla Industries, Inc. (Evansville, Ind.). A hot water heater, also shown at the exhibit, built by Sunworks, Inc. (Guilford, Conn.), could provide 100 gal—enough for an average family of four each day.

Since wind energy is in effect a form of solar energy, it is demonstrated by a 6-ft wind tunnel model. The wind system consists of a vertical-axis turbine mill with flexible blades for higher efficiency. The system, supplied by AT&T Sandia Laboratories (Albuquerque, N.Mex.), turns at 3 rpm, but can be accelerated to 30 rpm by a viewer's merely pushing a button.



## Frosting on the cake

A high-quality cake often has a fine frosting, and the exhibit provides the equivalent of this frosting. For example, viewers can operate a computer in which is stored climatic information, average number of days on which the sun shines, available energy in Btu/ft<sup>2</sup>, optimum angle for flat-plate collectors, values for resistance to heat or cold penetration of insulation ("R" values), and where to obtain more information. To have a readout of these data, the visitor has but to "punch in" his telephone area code and get a

# OUTLOOK

**Opening day.** Concern's Ignatius cuts ribbon while ERDA Administrator Robert Seamans and Concern president Margaret Mickey look on



readout in English, French, or Spanish.

Another frosting "flavor" is a light-reflecting sculpture powered by electricity from photovoltaic cells. The revolving sculpture was designed by Cambridge Seven Associates (Mass.), with cells by Jet Propulsion Laboratories (Pasadena, Calif.), and materials from Charles Maltbie Associates. Finally, one sees a cutout of a Stirling external combustion engine, able to provide motive power for electricity generation, which could be powered by a heat-concentrating solar collector tied into a high-temperature heat store.

Perhaps, however, the real frosting on

the cake is that the exhibit provides substantiation for the concept that energy independence and continued environmental improvement are not mutually exclusive. In providing a convincing argument for this concept, those who initiated, sponsored, and provided goods and services for the exhibit might be said to be in the vanguard of a new American Revolution—for energy and economic independence with a healthy environment—just as those who signed the Declaration of Independence 200 years ago were in the vanguard without which there would be no U.S. today. JJ



## Wastewater Samplers and Flowmeters

ISCO sequential and composite, portable or refrigerated samplers provide accurate timed or flow proportioned collection. High speed, valveless peristaltic pumps pass large suspended solids without clogging. Unsurpassed reliability in manholes is only one of the many ISCO advantages.

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# Flywheels: energy-saving way to go

In operation on subway cars today, flywheel technology may be used on private cars tomorrow to help you get to and from work and play in a less polluting way



Would you ride or drive a flywheel car? Fly what? A kite. No, a car that has a spinning wheel that stores mechanical energy that can be put in and taken out, much like water in a reservoir.

Such a car could use an electric motor

to store energy in a spinning flywheel. Or it might store energy from a conventional internal combustion engine in a spinning flywheel; this energy would then be used to propel the car. Using less gasoline, it would be one way to effect a fuel savings or substitution, in the case of the electric battery car. Rapid use of this technology is one step toward Project Independence, relieving U.S. dependence on imported oil.

To learn how such developments might be practical for the real world of daily urban commuting, the Energy Research and Development Administration (ERDA) will be spending nearly \$1 million in R&D studies in fiscal year 1977 that begins this month. Earlier, ERDA started its R&D in fiscal 1975; then in fiscal 1976 the federal agency spent about \$800 000 on flywheel technology.

George F. Pezdirtz, director of the di-

vision of energy storage systems, explains that the three-pronged goal of the ERDA energy storage activities are:

- conservation of fuel
- fuel substitution
- improved environmental quality.

"What ever this energy storage system division does it must satisfy these three requirements," he says.

Organizationally, the division consists of a chemical energy storage branch, a thermal energy storage branch, and a mechanical energy storage branch. The division is part of the Office of Conservation, one of six main offices in the ERDA.

## Why the interest?

The sudden interest in flywheels stems from a technical feasibility study on the subject by Rockwell International. Funded for \$152 000 with ERDA fiscal year '75 funds, the 1-yr study was completed this February. Referred to as a baseline study, it answered both technical and economic questions.

Last November, ERDA and the Lawrence Livermore Lab sponsored a 3-day flywheel technology symposium (Berkeley, Calif.) that drew more than 150 specialists from the flywheel community. Both the Rockwell report and the proceedings of the symposium are available from the Government Printing Office.

What will the federal energy office be doing with its funds—your tax dollars—to help solve the world's need for a nonpolluting vehicle?

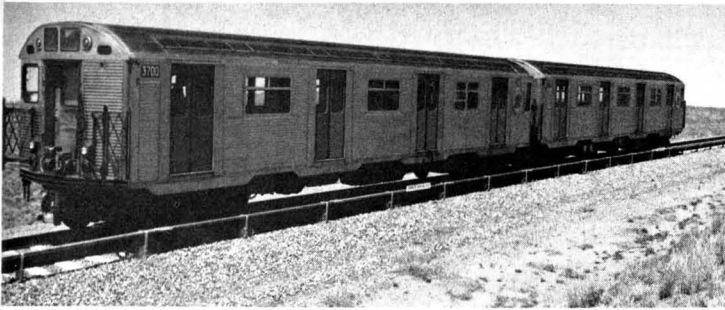
ERDA flywheel expert George C. Chang, chief of the mechanical energy storage branch, says that one of the major emphasis of his branch is on transportation; another is on utility applications. He says that there are several ways that the energy from a car engine can be captured and put to later use. All three are hybrid concepts; they range from a minor dependence to a total dependence on the flywheel. All three systems are being funded; ERDA is putting nearly \$1 million on a number of developments.

The first concept is that of regenerative braking; here the flywheel would play a minor role. The basic power of the car would come from a conventional internal combustion engine or perhaps an electric engine. "Here we are trying to design a flywheel, and the accompanying transmission requirements, that would capture

## Flywheel development today, at a glance

Technology application	Projects
• Subway rapid transit car	UMTA, <sup>a</sup> Air Research Div. of Garrett Corp.
• Electric trolley bus range extension	UMTA
• Flywheel/internal combustion hybrid car	Ford Motor Co., ERDA at University of Wisconsin
• Mine shuttle car	Bureau of Mines, Dept. of the Interior
• Switching engine	Federal Railroad Administration
• The urban car	Lear Motor Corp. and U.S. Flywheels use flywheels developed by Brobeck Associates of California
• Aircraft landing gear power boost	Rockwell International program supported by the Air Force
• Helicopter high-speed hoist	Lockheed program with Army support
• High-powered mobile equipment	DOD classified project totaling \$1.5 million
• Utility peaking	Public Gas and Service Co., of New Jersey with Battelle; Brobeck Assoc. (Berkeley, Calif.)
• Aircraft catapult	U.S. Navy program with all steel flywheels
• Advanced flywheel technology	NSF, Applied Physics Lab., The Johns Hopkins University

<sup>a</sup> UMTA, Urban Mass Transit Administration in the Dept. of Transportation



**Subway car.** Energy savings of 30% have been demonstrated with flywheel units

the energy lost from a moving vehicle resulting from braking," Chang explains.

ERDA is working with the electric jeeps of the Post Office on the regenerative braking concept. Ultimately, an improved performance of these jeeps is anticipated by incorporating flywheel-related technology into the vehicles.

The second concept, a flywheel-heat engine hybrid, is intermediate in its use of flywheel technology. This hybrid would rely about 50% on flywheel technology; a gasoline engine would be used to charge up the flywheel.

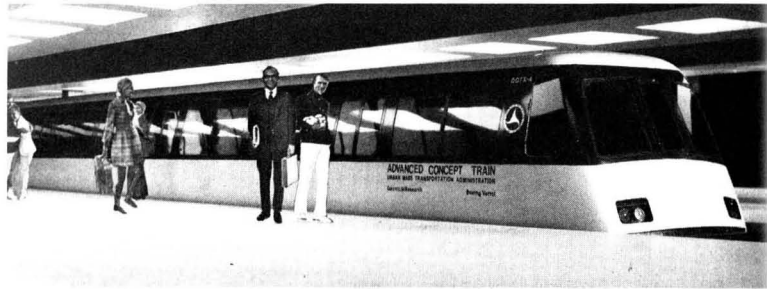
"In this case," Chang says, "one runs an engine such as a conventional internal combustion engine (ICE) under optimum conditions, to charge the flywheel." He explains that such a hybrid would get the best mileage from gasoline because the engine would be run at its best efficiency, which is somewhere between 45-50 miles/h—a condition under which no one wants to drive down today's highways.

Putting the energy equivalent of gasoline into perspective, Chang tells *ES&T* that today's ICE converts only 12% of the energy in gasoline to motive power. A dollars worth of gasoline gets 12 cents worth in energy. Chang estimates that flywheel hybrid development could up that energy efficiency to more than 20%, and theoretical efficiency is even higher than that. The ultimate third concept would rely 100% on the flywheel. Essentially, it would be a flywheel-only car.

**Funding**

With their fiscal year '76 funds, ERDA awarded a \$200 000 contract to the Lear Motor Co. (Reno, Nev.) for development of flywheel technology for possible use in commuter cars. Already, Lear Motor Co. has teamed up with U.S. Flywheels, Inc. (San Juan Capistrano, Calif.). This development is aimed at the ultimate hybrid, the 100% flywheel car. Earlier, the Lear Co. was in the great steam car race (*ES&T*, June 1972, p 512).

Other awards include \$125 000 to the Sandia Laboratory (Albuquerque, N. Mex.), which is looking at the heat engine hybrid vehicle, the second concept. Investigation started earlier with fiscal '76 funds. As



**ACT-1.** A new car from the wheels up, the advanced concept train uses flywheel unit

part of this contract, Sandia will be making an assembly of different rotors to help visualize the flywheel concept.

**Materials**

"Without any doubt the real advance in flywheels will be in materials and designs," Chang says. The Lawrence Livermore Lab (\$50 000 in fiscal '75 and \$270 000 in fiscal '76 funds) is looking at advanced composite flywheel rotors. "In the past, nearly all flywheels were made of metal," he explains. "The way to compare flywheel rotors is in terms of energy density—on the basis of watt-hours per pound (Wh/lb) of material." A typical state-of-the-art metal rotor would have an energy density of 3-14 Wh/lb. Within the next 10 years improvements in metal rotors can only increase the energy density to 5-15 Wh/lb.

"The real advance would be in the area of composite rotors made of plastics, fibers, and the like," Chang continues. "Here the state-of-the-art is in the energy density area of 10-20 Wh/lb but within 5 years it could be up to 30-40 Wh/lb and within 10 years to 60-70 Wh/lb."

A typical composite rotor is made of Kevlar, an aramid (aromatic polyamide) fiber made by Du Pont. It has, for example, a high volumetric density but is at the same time very light. Such a combination in rotors leads to more energy per pound of flywheel weight.

**Other activity**

All told, the federal government now has announced about a dozen RFP's (request for proposals) on flywheel technology totaling more than \$10 million.

David Rabenhorst, a scientist at the Applied Physics Laboratory of The Johns Hopkins University, has been working in the flywheel area for the past eight years. Some six or seven basic patents on flywheel technology have been issued to the APL/JHU. By now, he has made presentations to all major U.S. automobile manufacturers as well as the Lear Motor Company.

Rabenhorst's leadership in this area of technology is well known to every practitioner of this art. Anyone researching the literature in this field finds the name Rabenhorst as a first source of information on the subject of flywheels. He is now writing a book on flywheels that will be published next year by McGraw-Hill.

Rabenhorst explains that only three things count in a flywheel—the strength



**ERDA's Pezdirtz**  
"three requirements of energy storage"



**APL's Rabenhorst**

*"flywheels from almost any material"*



**UMTA's Mora**

*"options with flywheel use"*



**UMTA's Silien**

*"returning energy to the third rail"*

of the material, density of the material, and the configuration of the flywheel.

Kevlar, that wonder material used in belted automobile tires, has an ultimate tensile strength of 400 000 psi, Rabenhorst explains. Typical materials in the literature have tensile strength to 220 000 psi.

But Rabenhorst is interested in making more advanced flywheels less expensively. For example, he is interested in a bare-filament flywheel for which patent applications are pending; it is referred to as a string flywheel. It has no matrix yet a strength of 400 000 psi. "The string or filaments are tied at strategic places," he explains. When a flywheel is spun the centrifugal force causes a disc configuration to move as many as eight times sideways from its original position. In some cases, this movement causes the flywheel to break up; the filaments break away from the composite material in which they were imbedded.

Rabenhorst says that flywheels can be made from any monofilament polymer such as Dacron, Nylon, and even from such materials as cotton, steel wire, and wood fiber. He foresees flywheels of several types—super high performance, moderate performance, and low cost. One day, the latter might be made from paper, concrete—almost any material not costing more than a penny a pound.

### Testing

"We have already demonstrated the feasibility of a flywheel having an energy density of nearly 100 Wh/lb in full size spin tests with a 30-in. flywheel," Rabenhorst says. "We did this by spinning a 32-in. rod-shaped rotor in a 3-ft vacuum chamber." In this case the rod was made from Kevlar, the filament material called Flex Ten that Goodyear uses in automobile tires and for parachute tape. "Spinning this rod at 40 000 rpm in a vacuum chamber is equivalent to a flywheel rotor having an energy density of 60 Wh/lb," he says. "When the configuration of the rotor

is thin concentric rings, then the energy density would be 95 Wh/lb."

As part of the APL/JHU work funded by the National Science Foundation, the laboratory is building a flywheel assembly test rig. The APL/JHU rig will have an air turbine drive and a capacity to spin up to a 200-lb flywheel and up to 100 000 rpm, but obviously not each variable at the same time.

Moderate cost flywheels, those with an energy density of 20 Wh/lb and made from materials costing \$4 per pound, have been spun at the laboratory, Rabenhorst says. He explains that the rotors were made of fiber glass-plywood and that the energy cost would be 5 Wh/dollar.

Rabenhorst says, "We can build flywheels having a configuration of 100 rings." For practical reasons, these flywheels are 30-in. in diameter. The 100-ring configuration would be cheaper to make than one with five rings because it allows a simple ring attachment method to be used, according to the APL scientist.

In this case, the flywheel takes advantage of the thin-shell, filament-winding technology that was perfected under the space program. Such filament-winding technology was used to make solid rocket motor cases, which need light weight and high tensile strength; both specifications are needed for flywheels also. The 100-ring flywheel could be made from a thin-walled tapered shell similar to a filament-wound rocket motor case simply by slicing the many rings from the shell.

### Uses

Rabenhorst says that the Russians have flywheel buses and flywheel wind mills in operation today. In fact, the Soviets established a Mechanical Energy Recuperation Laboratory in 1965, that is currently under the direction of Dr. Nurbei Gulia. Flywheel technology could be an area of future environmental cooperation between the U.S. and the U.S.S.R. (*ES&T*, May 1976, p 414).

Rabenhorst says that the only thing that

will make the electric car attractive to the purchasing public is the incorporation of a flywheel into the battery car. He explains that the usefulness of a lead storage battery is dependent on how fast energy is drawn off the battery. The disadvantages of the present electric cars—limited range and poor acceleration—can be overcome. By using a flywheel in the car, the battery energy would only be drawn off slowly and intermittently. Such a flywheel-electric hybrid could use the lead battery conveniently. In this arrangement, the electric car would also have an infinitely variable transmission.

Putting flywheel technology in perspective, Rabenhorst says that earlier flywheels such as those used on buses in Switzerland and the Belgian Congo were in the operational energy density class of 1.25 Wh/lb. In Switzerland, a fleet of flywheel-powered buses were operated during a 17-yr period, ending around 1948. These buses were limited in distance between bus stops.

"When the public comes to realize that flywheels with an energy density of 40 Wh/lb are possible, then it will begin to appreciate the mechanical advantage of flywheels," Rabenhorst says.

### Rail rapid transit

Energy storage or flywheel research and development projects of the U.S. Department of Transportation's Urban Mass Transportation Administration (UMTA) began in 1971 with the award of a grant to New York's Metropolitan Transportation Authority to equip two conventional rapid transit cars (R-32 type) with a unique energy storage propulsion system.

According to Joseph S. Silien and Jeffrey Mora of UMTA's Rail Technology Division, the energy storage system captures a portion of the vehicle's kinetic energy during braking. Normally, this energy is wasted as heat released through underfloor resistor grids, but in the energy storage system the energy is stored in

spinning flywheels. The stored energy is then used to supplement third-rail energy requirements during vehicle acceleration. The primary objective of the project is to measure the energy consumption of the flywheel-equipped cars and compare the results with conventional systems.

Each of the two transit cars was retrofitted with a solid-state chopper control system, new separately excited traction motors (4 per car), and energy storage units (2 per car). Each energy storage unit contains four flywheel discs, a motor, and an alternator. The flywheels spin up to a maximum of 14 000 rpm.

In 1974, the cars were tested on UMTA's Rail Transit Test Track, a 9-mile electrified loop, at DOT's Transportation Test Center (Pueblo, Colorado). The cars were then tested in 1975 in non-revenue service on the New York City transit system, and went into revenue service on the BMT and IND Divisions January 29, 1976. The cars will operate for six months, and a final report will then be published on the results of the project. The total funding for the project was \$1.8 million from UMTA, and \$0.6 million from New York State's Department of Transportation and the Metropolitan Transportation Authority. UMTA spokesmen noted that energy savings of 30% have been recorded on test runs of the flywheel cars.

Why are transit authorities interested in flywheel systems? Mora explains that a transit authority pays for electricity based on its peak use with the maximum number of trains in service. If a line or a system is equipped with energy storage cars realizing a 30% reduction in energy consumption, there would be a reduction in power demand during the peak period. Therefore, both power consumption and power cost would be reduced.

The power bill of the New York City Transit Authority (UMTA) jumped from \$30 to \$80 million following the mid-1973 oil embargo. The NYCTA estimates its power costs could be reduced by \$20 million annually if all of its nearly 7000 cars were equipped with the flywheel/energy storage system.

In addition to the New York project, UMTA is undertaking development of two rapid transit cars representing dramatic technological and design innovation. These cars, known as the Advanced Concept Train, ACT-1, will utilize an advanced energy storage/flywheel propulsion system. Garrett AiResearch (Torrance, Calif.) is the developer of the ACT-1 and New York flywheel systems.

The objectives of the ACT-1 project are to advance the state-of-the-art of rapid rail transit car design and construction, and to demonstrate the benefits of advanced technology when applied to existing and future rapid transit systems. In order to select a contractor for the ACT-1 cars, a design competition was held in 1972. Garrett was awarded the ACT-1 contract, largely as a result of its energy storage/

flywheel concept and associated operating cost savings.

There are significant differences between the ACT-1 cars and the R-32 cars operating in New York City today. Silién explains, "a chopper control will not be used on the ACT-1 eliminating high-powered, circuit-controlling electronics. Armature circuits and control with low power fields driven by phase delay rectifiers will replace the chopper control."

The R-32 system consists of four 2-in.-thick steel alloy discs bolted together as contrasted to 27 thin laminated steel alloy discs that are pressure mounted on the rotors of the ACT-1 cars. At present, the flywheel units for ACT-1 are undergoing acceptance tests at Garrett, and the two cars are in the advanced stages of construction. At the end of this year, the ACT-1 cars will be delivered to the UMTA Test Track for test and debugging. In late 1977, the cars will be evaluated under revenue service operating conditions on some of the transit properties.

A number of options become available with extensive use of flywheel-equipped transit cars. Reduction of power consumption and cost is the most obvious. Alternatively, a transit authority with ACT-1 equipment could increase the number of trains, put more in service yet pay the same electricity bill. Also, the authority could air-condition presently non-air-conditioned cars at no extra energy penalty.

#### Nonflywheel activities

Another way to save on energy, analogous to automotive regenerative braking, involves regenerative choppers, Silién notes. These units would put energy back into the third rail, but the ability of the line to absorb the energy would only be possible when a second train was in the vicinity of the one with regenerative choppers, or when there was a load on the line. Otherwise the energy would go to a resistor grid where it would be converted to heat and lost, as is presently the case.

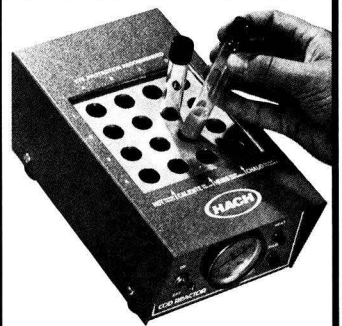
#### Checking it out

Built in 1970, the DOT test facility (Pueblo, Colorado) involves both the FRA (Federal Railroad Administration) and UMTA. UMTA's 9-mile Rail Transit Test Track has the capability of testing urban (or intercity) rail equipment at speeds up to 80 mph. The primary purpose of the track and the ancillary maintenance facilities is to serve as a reference for test and evaluation of urban rail vehicles.

A secondary purpose of the track is the test and evaluation of state-of-the-art and advanced track structures. For example, two different weights of running rail are used in the track (119RE and 100RE), and welded and bolted rail and both wood and concrete ties are used. The UMTA investment in track, maintenance, and administration facilities exceeds \$26 million.

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# Tracking the elusive pollutant

Field and laboratory data are being collected to assess and model the sources and sinks of man-made chemicals

Before the advent of the chemical era, man's domestic wastes could be handled adequately by biological degradation processes. However, with an almost unparalleled surge in creativeness, man has produced literally hundreds of thousands of "unnatural" chemicals that are resistant to biological oxidation processes.

Yet these synthetic creations—xenobiotics or anthropogenic materials in current parlance—must in some fashion be sequestered or decomposed to environmentally innocuous substances. The nonbiological modes of transportation and transformation of these man-made pollutants was the subject of a recent conference sponsored by the EPA, the National Bureau of Standards (NBS), NSF and ERDA.

This subject of study has stimulated the formation of a new Environmental Pollutant Movement and Transformation Advisory Committee and a program for the Assessment of Carcinogens in the Environment both within the EPA. At the international level, a speculative account of the **Economics of Transfrontier Pollution** (1976) was recently published by the Organization for Economic Co-operation and Development (OECD).

## The need to act

On the domestic front, of the hundreds of thousands of chemicals that have been produced in the laboratory only about 30 000 are of commercial significance, and only a small fraction of these are environmentally harmful. Since these latter chemicals are dangerous because they are persistent, concentratable, or may be transformed to more toxic forms, they must be prevented or limited from entering the environment. But first they must be identified.

Unfortunately, an adequate description of our pollution problems cannot be drawn until the details of pollutant transformation processes within air, water or soil, and the transport of toxicants between these media are known. Assessment and modelling efforts are in their infancy.

To tackle the problems, the EPA, within the structure of its Science Advisory Board, has established a 15-member pollutant movement and transformation advisory committee to assist the administrator in matters relating to a pollutant's entrance and fate in the environment. The committee will evaluate existing data on pollutant translocation, pollutant transmutation after interaction with other systems and the implications of these alterations on EPA rule making.

In an effort to develop early warning systems, the agency will monitor the presence and activity of suspected carcinogens in the various environmental media, under a 5-yr assessment program that has received an initial funding of \$1.1 million. The multiphasic effort, undertaken by EPA's Environmental Monitoring and Support Laboratory in Las Vegas, Nev., will assess media transport, inter- and intramedia transformation, measurement techniques and methods and exposure levels of man-made and natural carcinogens. Epidemiological and toxicological studies will follow.

In addition to the activities within the EPA, many basic research and modelling efforts are being undertaken at universities and private companies throughout the U.S. Excellent samplings of these latter efforts were presented at the conference held on the NBS campus this past May.

As was repeatedly emphasized at the conference, the ability to predict the fate in the environment of those pollutants resistant to biological degradation requires detailed information on the physical and chemical properties of the reactants (pollutants, water, soils), and the quantities of reactants and products involved under environmental conditions. Precise information of this kind is not available today, and the ultimate sinks for these xenobiotics are not yet fully predictable. Enough information from laboratory and field observations is at hand, however, to enable tentative attempts at modelling the fate of pollutants. But these initial mod-



**Water sampling.** Taking bottom sediment samples from Chesapeake Bay

elling efforts are not the sophisticated predictive creatures the scientists working in this area eventually hope to develop.

## Fate in an aqueous medium

As a general rule, most harmful organic xenobiotics can, over time, be detoxified as a result of their susceptibility to attack by physical and chemical processes (see box) in an aqueous environment. Such is not the case with trace metals, however, and these substances must be sequestered or buried out of harm's way.

The physical mechanisms are all expressions of the pressure to escape from the aqueous to a gaseous or solid phase. Available evidence suggests that volatilization may be the primary route for the transformation of low-molecular-weight organics such as benzene and dichloroethane, while precipitation may be the major pathway for polynuclear aromatic hydrocarbons. Adsorption, on the other hand, may be the principal mechanism accounting for the transport of trace metallics and other non-volatile organics into sediments.

Of the possible chemical pathways—all of which are affected in their rates of reaction by temperature and pH—direct oxidation by oxygen appears to play the least important role in the transformation of aquatic xenobiotics. As a general rule, an organic pollutant that is readily susceptible to direct oxidation by oxygen is even more susceptible to biological oxidation. Oxygen, however, may play a reoxidizing role in some reactions.

The significant role that light plays in the transformation of organic materials in water has been surmised for years. What remains clouded in mystery are the mechanisms involved. In photolysis, for example, the pollutant behaves in a self-



destructive manner: It absorbs light, which leads to its decomposition into more reactive fragments—free radicals—that engage in oxidation through radical chains. When excitation of the pollutant by light results in the formation of singlet oxygen, a more active oxidizer than oxygen, the process is termed photochemical oxidation. If the formed singlet oxygen then initiates the oxidation of a substance other than the original excited pollutant, the process is called photosensitized oxidation. Metallic complexes of nitrilotriacetate, benz(a)pyrene, 2,4-dichlorophenoxyacetic acid and pesticides are examples of compounds that undergo light-induced transformation reactions.

For esters—phthalates and phosphates—hydrolysis is the important transformation mode. Hydrolytic reactions of these organics are acid-base catalyzed and, therefore, pH dependent. The products of hydrolysis—organic acids and alcohols—can be efficiently attacked by biological mechanisms and complete degradation of the initial pollutant usually occurs.

### Macromolecular world of soils

Once you leave the aquatic environment and enter the complex media of soils and sediments, distinctions between biological and chemical reactions become very subtle. One exception is field-applied pesticides, the most closely studied class of pollutants to date.

For pesticides, the soil and sediment environments offer little opportunity for chemical decomposition, and microbial action and sunlight are generally assumed to be the major routes of degradation. Nevertheless, certain organophosphorus insecticides, Parathion (*o,o*-diethylparanitrophenylphosphorethiolate) for example, undergo hydrolytic reactions that are catalyzed by acids.

Even if direct evidence for chemical degradation is lacking, it can sometimes be assumed that chemical breakdown of a pesticide in soil has occurred if suitable microorganisms are found to be absent. A case in point is the degradation of amitrole (3-amino-1,2,4-triazole) for which specific microorganisms capable of acting on this pesticide have not been isolated and identified.

Although it may be difficult to distinguish between biological and chemical mechanisms, it is logical to expect that a complex organic molecule is acted upon by a combination of both processes. Soil bacteria act upon organic molecules to degrade them to CO<sub>2</sub>, water, nitrogen and chloride ions in a self-cleansing process termed mineralization. The intermediates formed in this degradation process are complex molecules that may undergo purely chemical reactions to yield unexpected products.

The aniline-based herbicides are excellent examples of substrates for both microbial and chemical action. These

herbicides are attacked first by microorganisms and are slowly degraded to CO<sub>2</sub>. However, also detectable in the soil samples are azobenzenes that could only have been formed from the chemical condensation of two molecules of aniline.

Another main pathway for chemical decomposition is reduction. In the laboratory, toxaphene and DDT have been shown to undergo reductive dechlorination when the conditions were made strongly anaerobic and the soil was flooded. Under these same conditions, dinitroaniline herbicides can be nonbiologically degraded to *m*-phenylenediamine. That these types of transformations occur in natural sediments under anaerobic conditions (deep soil strata) is feasible, but direct evidence is still lacking.

### Power of the sun

Ultraviolet radiation from sunlight is sufficiently energetic to bring about photochemical transformation of xenobiotics dispersed in natural environments. Photochemical reaction types are numerous (see box) and complex.

The growth regulator *p*-chlorophenoxyacetic acid undergoes oxidation, reduction and photonucleophilic displacement reactions during its decomposition to a dark quinol polymer. Under the influence of sunlight, the herbicide Monuron [3-(*p*-chlorophenyl)-1,1-dimethylurea] is oxidized and then hydrolyzed to *p*-chloroaniline, which is further oxidized to azobenzene or *p*-chloronitrobenzene. A prime example of a pesticide that undergoes isomerization during degradation is dieldrin.

As can be inferred from previous discussions, a pollutant's ultimate environmental impact, whether it is attacked and detoxified biologically, chemically, physically or photochemically, is directly related to its concentration, its physical-chemical state, its interactions with other

components of the microenvironment that has entered, and even its mode of entrance to that environment.

### Mathematical modelling

The chemistry and physics of complex compounds are often well understood. But the sources and sinks for these compounds are often unknown or poorly definable because they are dependent on a myriad of external factors such as pH, temperature, sunlight, and soil composition. Mathematical evaluative models can be designed to describe the behavior and fate of substances under specific environmental conditions. But the basic difficulty confronting the modeller is the uncertainties involved in expressing accepted chemical, physical and biochemical reactions in the context of a complex natural system.

The modeller usually finds that, although some questions can be solved theoretically, most problems require direct field observation and laboratory experimentation for solution. Often he finds that he must alter his original conception to conform to his observed on-site or laboratory results.

Most models that describe the transport or transformation of pollutants are restricted by design or current knowledge to a limited physical space or one environmental medium. One model, the Wisconsin Hydrologic Transport Model (Patterson, M.R. et al., ORNL/NSF/EATC-7, 1974), addresses the transport of heavy metals on a larger geographic scale—a watershed scale—and considers pollutant transport through water and soil. Through the linkage of several submodels, a variety of processes—solubilization of the pollutant by precipitation, the initial infiltration into soil, evaporation and transpiration processes and sedimentation of the pollutant once it reaches the stream channel—important to watershed transport can be described.

This model considers the source of pollution, how the pollutant is injected into the ecosystem and the pathway of injection (aerial or terrestrial), whether the origin is point or area source in nature and whether the pollutant is directed to the surface of the land or injected directly into the hydrologic system. Transport of particulates entrained in water by soil erosion processes and by direct deposition into the water can thus be modelled.

To make the Wisconsin system more complete, other models can be coupled to it. For example, models of plant growth can be linked to it in order to assess the effect of growth rates caused by an entrained pollutant, and the uptake of that pollutant by the plant.

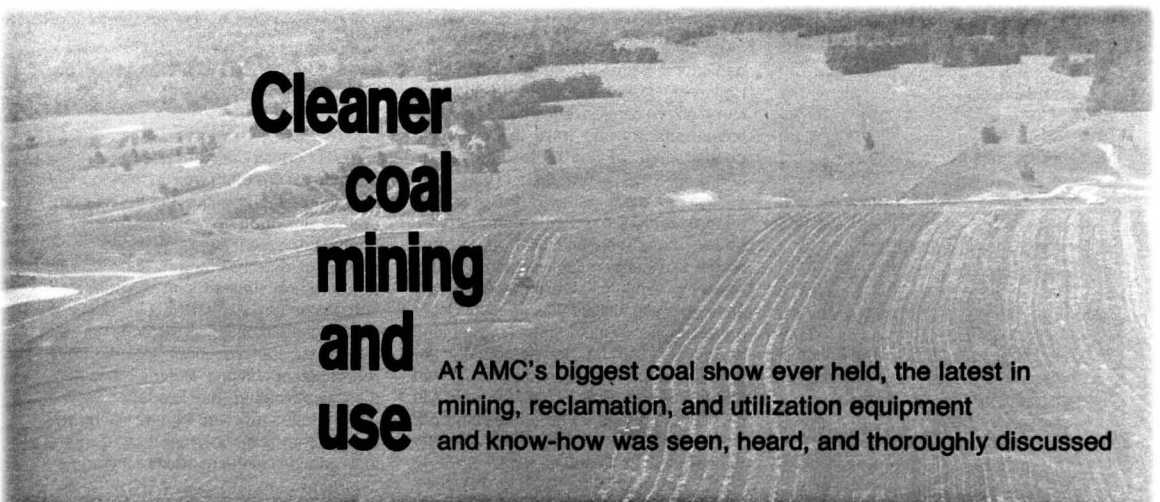
The Wisconsin model, like many of the other less extensive models discussed at the NBS conference, is constantly being readjusted to conform to more recent information gathered by the modeller in his quest of the elusive pollutant. LRE

## Processes acting on pollutants resistant to bio-oxidation

CHEMICAL  
Hydrolysis  
Direct oxidation by oxygen  
Catalyzed oxidation  
Photolysis  
Photooxidation  
Photosensitized oxidation  
Condensation

PHYSICAL  
Volatilization  
Precipitation  
Adsorption

PHOTOCHEMICAL  
Oxidation  
Reduction  
Photonucleophilic displacement  
Elimination  
Isomerization



# Cleaner coal mining and use

At AMC's biggest coal show ever held, the latest in mining, reclamation, and utilization equipment and know-how was seen, heard, and thoroughly discussed

**Illinois wheatfield.** *This was once a surface mine*

It was the mid-1940's, and World War II was at its height. In the U.S., petroleum-based fuels, particularly gasoline, were rationed, or otherwise carefully husbanded. During that time, a young Democratic Congressman from West Virginia, Jennings Randolph, rode in a car in Pittsburgh, Pa., and later, in a small aviation "gas"-fueled airplane from West Virginia to Washington, D.C.

The point that Randolph, now a veteran Senator, made to a press conference organized by the American Mining Congress (AMC, Washington, D.C.), was that the "gas" used to fuel the car and plane was made from coal. He noted that the petroleum "crunch" of World War II led to concerted research into synfuels from coal, but that this research petered out by the early 1950's when inexpensive petroleum was once more available. Randolph also complained that the lesson of the 1973-1974 oil embargo was not really driven home, and warned that the lack of momentum in synfuel development could well result in the U.S. being in a worse "fix", should a new oil embargo occur.

The press conference at which the Senator expressed these views was part of AMC's 1976 Coal Show held at Cobo Hall, Detroit, Mich., in May. The largest show of its kind ever held, it contained exhibits of over 300 manufacturers, and hosted about 18 000 registrants from all over the world. J. Allen Overton, Jr., president of the AMC, said.

## Getting the coal out

Whatever the ultimate use of coal—be it for steam, metallurgy, or synfuels—the coal must be mined from the earth, and, as Secretary of the Interior Thomas Kleppe reminded Coal Show attendees, the goal is to mine at least 1 billion tons by 1985, up from the 1975 output of 640 million tons. Of this 1 billion or more tons, about 305 million tons would be produced from federal lands, with the major portion surface-mined.

Meeting this goal "means coming to terms on satisfactory compromises that will produce coal and . . . protect the environment", Kleppe said in his keynote address. He expressed his confidence that both can be done within the framework of the National Environmental Policy Act (NEPA) and the Mining and Minerals Policy Act, which he called "compatible and complementary". With respect to surface, as well as underground mining, particularly in the West, Kleppe explained that new regulations, published by his department in May, are as strict, or stricter, on balance, than twice-vetoed surface-mining bills approved by Congress, but that they "have a flexibility [lacking in the bill, H.R. 25] that would allow us to function".

To emphasize Kleppe's point, copies of "Surface Management of Federal Coal Resources" (43 CFR 3041) and "Coal Operating Mining Regulations" (30 CFR 211), issued by his department, were handed out at a later Coal Show press conference. The rules embodied in these two documents are aimed at ensuring that "only those federal lands that can be mined in an environmentally sound manner are mined", while the President's objective "to make available for production vast stores of our own domestic energy resources" is met. The first set of regulations comes under the jurisdiction of the Bureau of Land Management (BLM), and the second is in the bailiwick of the U.S. Geological Survey (USGS). They apply to 537 federal coal land leases (799 000 acres with about 16.4 billion tons of recoverable coal), most of them on western coal lands.

## Soil reconstruction

The future will see increasing requirements for reclamation of surface-mined land after the recoverable coal is taken, but each site or region will have problems peculiar to it. For example, techniques of reclaiming land in Pennsylvania or West

Virginia, generally blessed with favorable soil, water, and rainfall conditions, would differ sharply from techniques required for more arid areas, such as Montana, North Dakota, or Wyoming. However, the common denominator is that the restored land should be made useful for agriculture, recreation, wildlife habitat, or other purposes. Therefore, surface-mine overburden cannot merely be dumped into the hole and shaped to contour; the type of soil for revegetation of this land must be taken into account.

Donald McCormack, a soil scientist with the U.S. Department of Agriculture (USDA), told a Coal Show technical session that since about 1950, detailed soil surveys have been completed for nearly 60% of the U.S., with approximately 11 000 "soil series" classified, defined, and mapped. Each soil series is actually a unit that has specifically defined, relatively narrow property ranges. Knowledge of the type of soil series at a potential surface-mine site would certainly facilitate engineering estimates as to whether regrading and planting the soil for reclamation would be relatively easy and inexpensive, or difficult and expensive, or whether the surface mining should not be undertaken at all. This knowledge is of great importance when one considers that more than 4 million acres in the U.S. have been surface-mined—not only for coal—and that such mining is proceeding at more than 100 000 acres/yr for coal alone; however, for most of this acreage, reclamation is, or will be undertaken.

Most recent state laws require return of original topsoil to the mining site. Virtually all coal states have such laws. McCormack said that this topsoil should consist of the organically enriched "A" horizon, usually 4-25 in. thick and most conducive to revegetation. By contrast, the subsoil or "B" horizon is higher in clay, gravel, or alkali content, and lower in organic matter, though it can perhaps eventually be brought "up to snuff"

through careful planting sequences. "C" subsoil horizons are even less favorable. Often, however, in reclamation, A and B horizons may be mixed (this mixture is often referred to as reclamation "topsoil"), or, worse, both horizons could end up partly or wholly buried under mine overburden if due care is not taken.

McCormack listed 10 recommended steps for soil reconstruction. Among these steps are

- detailed soil surveys at the site
- learning what overburden strata will be exposed, how they will be mixed, and whether any are objectionable or toxic
- separate stockpiling of the A horizon
- mining with burial of any objectionable strata
- spoil, B horizon, and A horizon grading and seeding.

He called for further development of techniques to improve soil reconstruction, and gave suggestions for cost reduction. It is difficult to make a general quantification of these costs and their reduction, because sites and their characteristics vary widely.

Edward Greenwald, Jr., of Resource Engineering and Management, Inc. (Pittsburgh, Pa.), a landscape architect, advocated use of the "design process" with respect to surface mining. The design process is a six-phase effort which, among its phases, calls for exhaustive site inspection and reconnaissance, and collection and analysis of all environmental data, including soils, biota, climate, land use, drainage, and subsurface conditions. Greenwald said that the design process is not complex, and will offer approaches that "generally reflect a balance between economy and environment", especially important in view of the increasingly stringent regulations which he foresees for the mining industry.

#### Coal preparation and use

If coal is burnable in an environmentally acceptable manner, it costs less than \$1/10<sup>6</sup> Btu for power generation. Thus, if all oil and gas power plants converted to coal, consumers could save \$5 billion/yr. U.S. Bureau of Mines scientists W. E. Warnke and A. W. Deurbrouck said in a Coal Show technical paper.

The key words, however, are "environmentally acceptable", and that means burning coal to meet clean air standards by flue gas scrubbing, or by preparation of coal before burning. Coal preparation was economically absurd when oil sold at the wellhead for \$2.50/bbl and gas for 29¢/10<sup>6</sup> Btu. Thus, it would have been folly to spend more than a few cents/ton of raw coal to remove some coarser ash and pyrite particles. \$11-\$13 oil changes this picture.

Thus, the time for more thorough coal preparation has come, but its state-of-the-art lags behind that of processing of metallic and nonmetallic minerals, the BuMines scientists pointed out. Nevertheless, the incentive for a rapid technological advance in steam coal cleaning is there, partly because of clean air regulations, and partly because today's coal prices provide some economic justification.

One preparation approach is washing, and BuMines tried this method with 445 steam coal samples from working mines. The coal averaged 3.02% S (1.91% pyritic sulfur), 14% ash, and 12 574 Btu/lb. This works out to 4.8 lbs of SO<sub>2</sub>/10<sup>6</sup> Btu from the stack; new source performance standards call for 1.2 lbs of SO<sub>2</sub>/10<sup>6</sup> Btu. Thus, a formidable sulfur problem exists, and it can be worse for certain midwestern coals.

The coal can be ground to -28 mesh. This ground-up coal can be subjected to BuMines' improved froth flotation procedures with high-ash refuse and coarse pyritic sulfur removed as tailings. The coal froth concentrate is repulped in fresh water at a pH of less than 7. A pyrite collector and frother are added to the float, and a coal depressant is introduced. The pyritic material goes out with the froth, and a clean coal underflow, with up to 90% of pyritic sulfur removed, is collected. BuMines is also looking into other approaches, including new magnetic techniques, and is working on methods of making lignite more acceptable, as well as drying coal with less emission to the air.

#### Where there's smoke . . .

Show attendees were reminded of danger of fires and smoke pollution from refuse piles resulting from mining and preparation of coal. David Maneval, science advisor to the Appalachian Regional Commission (Washington, D.C.), said, however, that newer mining practices will probably slowly reduce the scope of this air and solid waste problem in the future. The reworking of these piles for carbon values could help even more.

Nevertheless, in Pennsylvania alone, there are believed to be 200 such burning piles. A 1963 estimate of almost 500 fires in the U.S. may still be fairly accurate this year because of new fires starting, while others are put out through government and private efforts, or simply burn out. In 1969 dollars, to extinguish such a fire could cost 50¢-\$2/ton, Maneval said, while a properly constructed safe pile might cost 5-50¢/ton. Maneval also explained what conditions are most condu-

cive to fires, and discussed extinguishing techniques.

#### What hopes for synguels?

By 1985, 2.5 million bbl of oil/day were planned to be synthesized from coal. ERDA's present estimate is that virtually zero bbl/day of oil will be made from coal by that year, and only 250 000-500 000 bbl/day oil equivalent of gas (original plans were for 0.5-1.5 million bbl/day oil equivalent), according to figures compiled by the General Accounting Office (GAO). These figures disturbed Sen. Randolph, who held his first press conference ever, since his initial service in Congress in 1933, at which he called for the estab-



**Interior Secretary Kleppe**  
*Issued surface mining regulations*

lishment of an Office of Synthetic Fuels Commercialization under ERDA. He is confident, however, of passage of a loan guarantee bill for synguel development during the present session of Congress.

In any case, aside from conservation, coal remains the "quickest-fix" approach for the U.S. to alleviate its energy bind. However, AMC president Overton warned that certain proposed legislation could restrict coal production and halt expansion in some thinly populated U.S. areas. He emphasized that mining companies—most of whose people appreciate a clean environment as others do—"are committed to surface mining only where the land may be restored to beneficial use". He urged that governments remove roadblocks so that the U.S. can use abundant domestic coal to lessen reliance on uncertain foreign sources of energy supply. JJ

# Poisoning

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Since the classical period of Greece, lead has intermittently been recognized as a health hazard. However, current awareness dawned only about a hundred years ago, while extensive scientific investigation began even later, around 1930. This research, far from being limited to the health sciences, has encompassed a wide and diverse variety of disciplines, and has generated an overwhelming number of articles, papers, and reports. Even extensive review articles cannot completely summarize most subtopics in lead research. And, in too many instances, it is apparent that the author was unaware of previous related or identical work; consequently, much duplication exists.

This overview addresses the biological impact of lead—its environmental transport to man and its effect on man—and serves as a guide to the best sources of information currently available. Topics on chemistry, analytical techniques, and measurement problems are not included except where they are incorporated in a biologically oriented presentation.

## **Review projects, symposia**

The voluminous quantity of published information on lead makes it impractical to collect a comprehensive bibliography for any new research venture. Fortunately, several excellent annotated bibliographies and reviews have been published that provide a reasonably extensive and readily attainable data base for a background investigation.

**Biological Aspects on Lead: An Annotated Bibliography** (EPA, 1972). This comprehensive two-volume compilation of literature on lead covers the years 1950–1964. Its 4103 entries are organized into ten parts by subject and, within each part, by year of publication. Some topics covered include:

- lead in the environment, including contamination of food and water from both natural and man-made sources (Part II)
- medical aspects of lead in man (Part IV)

- industrial atmospheric and occupational lead exposures (Part V)
- lead pollution in air, soil, and water, and the effects of such on humans, animals, and plants (Part VI)
- legal matters, regulations, recommendations for threshold and maximum allowable concentrations, and food and water standards (Part VII).

The review ends with an author index and an excellent subject index. The scope and completeness of the material more than compensates for the lack of any discussion of the topics abstracted.

Perhaps by this time much of the material published prior to 1950 can be considered primarily of historical interest; however, it may often be helpful to tap this extensive store of knowledge, particularly for the period 1930–1950. Apparently there are adequate historical treatises available on lead toxicity in Colonial America, but only essays on isolated situations exist for other historical periods and places.

**Lead and Air Pollution: A Bibliography with Abstracts** (EPA, 1974). This 431-page document is an extension of the above annotated bibliography. Covering material published through 1972, it contains over 1800 abstracts and a comprehensive author and title index, and is intended only to be representative of the available literature. It contains a higher proportion of non-English language references and covers a wider range of lead topics. It is divided into fourteen categories: two categories on biological effects and the remaining twelve on sources, control, measurement and basic technology.

The publishers of this document, the EPA's Air Pollution Technical Information Center, also publish a monthly bulletin, "Air Pollution Abstracts," which contains over 6000 abstracts per issue on all aspects of air pollution. However, since the biological effects of lead constitute only a very small fraction of its content, this bulletin should not be considered a routine source for biological references on lead.

**Poisoning and Intoxication by Trace Elements in Children** (DHEW, 1973). This is a much less extensive annotated bibliography for the years 1966–1971. It is divided into six topical sections and has an author and subject index. Only about 15% of its 247 references deal with toxins other than lead. Its principal



## In search of the facts

A guide to the best information on the biological impact of lead on man is offered to aid the scientist venturing into this area for the first time

limitation is that it covers only the medical aspects of lead poisoning in children; adult exposure, exposure routes, environmental transport, animal experimentation, or lead distribution and metabolism are topics not discussed.

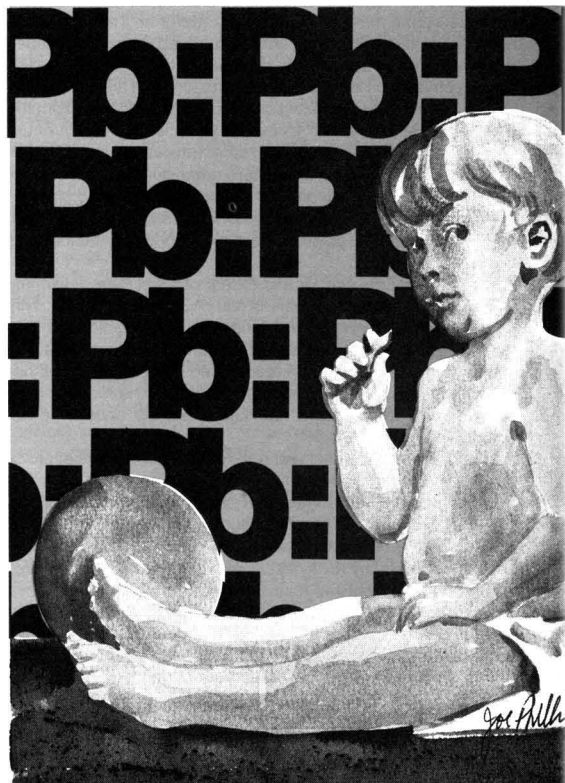
"Lead Poisoning" (*Sci. Am.*, 1971). This concise and well-written review essay on the medical aspects of lead toxicity is not a research article and has only a six-item bibliography. But, it does serve to inform those who are not actively involved in lead research.

**Lead: Airborne Lead in Perspective** (National Academy of Sciences, 1972). This comprehensive and scientifically oriented review contains nine chapters written by several contributors who cite 600 references. Written as a textbook on the biological impact of lead, this review is far from limited to airborne lead as one might gather from its title. Subject matter also includes the distribution, uses, ecological transport, and chemistry of lead; the absorption and biological effects of lead in man; and the effects of lead in animals other than man.

An excellent general summary and recommendations for further research are presented and the extensive appendices detail some of the methodologies presently being used. This work adequately reviews the currently important aspects of lead toxicity, and its list of contributors is valuable for literature searches by author.

**Symposium on Lead** (*Arch. Environ. Health*, 1964). This symposium is a collection of 18 articles by different authors. The first series of articles discusses the uses, occurrences, distribution, and chemistry of lead. The next series discusses the metabolism and clinical aspects of lead toxicity. Another series of articles discusses organic lead as a gasoline additive and its emission to the environment in automobile exhaust. Air quality and the epidemiology of lead exposure are discussed in concluding articles.

**Technical, Intelligence, and Project Information Systems for the Environmental Health Service; Volume III, Lead Model Case Study** (NTIS, 1970). This Battelle Institute report describes a mathematical model of the transport and distribution of lead in the environment and in man. In the process of gathering the information necessary to quantitate and use the model for predictive purposes, the lead literature was thoroughly reviewed.



The first 30 pages of the report contain a detailed discussion of this "information base" and is an excellent source for quantitative data. Additionally, about 600 references are cited in a categorized bibliography.

The report begins with a discussion of the natural occurrence of lead, its refining and uses, and the environmental exposure experienced by man. It then gives a detailed discussion of the biochemistry (metabolism, storage, and toxicology) of lead in both adults and children. Many excellent tables summarize the worldwide distribution of lead and the epidemiology of its effects. The report also includes recommendations for future lead research.

**Implications of Airborne Lead** (EPA, 1973). This review, similar in scope and organization to the Battelle report but minus the mathematical model, cites about 150 references, although they are based on personal communications and about one fourth cite **Lead: Airborne Lead in Perspective**. It contains a chapter on the hazards and importance of lead in dust. It is perhaps most useful as a summary and update of **Lead: Airborne Lead in Perspective**.

**Environmental Health Aspects of Lead** (European Communities, 1973). This is a compilation of the proceedings of the most ambitious project on lead to date, the EPA's International



Symposium held at Amsterdam in 1972. The chief value of this publication lies in the detailed descriptions of many specific lead pollution incidences, especially those in Europe. However, its presentations of health hazards, environmental transport, and monitoring techniques are limited

**Symposium on Biological Effects of Heavy Pollutants** (*Clin. Toxicol.*, 1973). This short, excellent and comprehensive document reports research presented to the research section of the American Veterinary Medical Association in 1971. Its authors discuss the extrapolations from animal to man and use much of the research in man as bibliographic material. This collection is essential to anyone using animals for lead research because it details the species variation in response to lead. It also shows how a combination of effects in several different animal species can be used to reproduce all the effects of lead in man from the inhibition of red blood cell formation (rabbits) to the pica of underprivileged children (dogs). A rather interesting case of seasonal variation is also reported; here urban dogs show the same seasonal variation in blood-lead concentrations as do children living in the same geographical areas. This veterinary symposium does not, however, discuss the production, distribution, and transport of lead.

*Estimates of the Nature and Extent of Lead Paint Poisoning in the United States* (National Bureau of Standards, 1972). This comprehensive survey of the epidemiology of childhood lead toxicity in the U.S. evaluates the magnitude and extent of poisoning from the ingestion of lead-based paint by using mathematical models. The information upon which the models were based, along with a partial validation and the underlying assumption, are discussed.

Not all these symposia and reviews are needed to research the work done on lead because many of these works overlap extensively in subject matter and research projects differ significantly in emphasis. The Battelle project is, in the opinion of this author, the best and most comprehensive review. The **Annotated Bibliography** (EPA, 1972), with its comprehensive index, is very useful to locate specific details for its time period. These two publications could stand alone as a compendium and source of original articles on lead's biological impact. **Lead: Airborne Lead in Perspective** can serve as an alternate and shorter, though less comprehensive review. Anyone interested in animal research should consult the veterinary symposium (*Clin. Toxicol.*, 1973).

#### Periodicals and other sources

The aforementioned symposia and reviews cover the lead research effort through about 1970. Since that time many articles have been published in a bewildering variety of journals. All the clinical (medical) journals contain articles on lead; the *New England Journal of Medicine* has published several particularly good ones. Journals with the words "environment" or "pollution" in their title contain articles one would expect in public health journals; in recent years the latter have published relatively few contributions from lead research. The toxicology and pharmacology journals contain many reports of lead research as do general scientific journals such as *Science* and *Nature*. Also, because most of the biological research on lead is performed with animals, any comprehensive search must include the veterinary journals.

If this author had to choose only one journal as a basis for reviewing the current research on the biological impact of lead, he would choose the *Archives of Environmental Health*. Although this journal cannot begin to publish all of the details for all fields of lead research, it is broad enough in scope to start a bibliographic search for many of these fields.

Since environmental distribution and transport data are usually published as special or government reports, it is essential to consult the catalogs of the Government Printing Office and the National Technical Information Service. Access to indices of the current research projects of the U.S. Environmental Protection Agency, the National Science Foundation, and the National Institute of Health would also be useful. In addition, it should



be noted that many libraries often catalog special reports and symposia proceedings.

### Information sources by topic

#### *Environmental transport and occurrence*

The distribution and transport of lead is a popular subject in the non-medical scientific literature. It is rather easy to find qualitative discussions of this field; however, quantitative studies are more difficult to obtain.

Recently, substantial work has been done on identifying sources of atmospheric lead by studying isotope ratios. Using this technique, one can determine such things as whether the lead came from gasoline or coal and, if from coal, where the coal may have been mined. Much of the recent isotope work has been reported in *Science* although *Environmental Science & Technology* also carries many of these reports. The symposia and reviews mentioned previously have very little information on isotope ratios, or on radiollead; an early review that discusses environmental and historical levels of lead was published by the Nuclear Energy Information Center (Warsaw, Poland, 1967).

For extensive information about exposures to lead in the vicinity of lead smelters, the EPA International Symposium proceedings report (1973) contains a number of individual reports, while the other symposia and reviews give only general summaries of these situations. The environmental journals also contain many reports of lead in the vicinity of smelters and lead processing factories. When these situations result in economic loss to cattle and horses, the veterinary journals publish them. The medical journals contain many reports of human occupational exposure, but these reports concentrate on individual cases and clinical aspects of toxicity; few are concerned with the geographical extent or epidemiological aspects of the hazard.

Papers that describe epidemiological studies report blood levels of lead. It is becoming increasingly evident that blood level, as distinct from absorption and dose, is not a good index of exposure. These reports tend to be in the medical literature; the *Journal of the American Medical Association* has a number of them. Such studies are enormous and are well summarized in the National Bureau of Standards report (1972).

Atmospheric lead is a most popular subject and has been for some time. All the symposia have extensive discussions of atmospheric lead—particularly with respect to that caused by automobile exhaust. Much of the emphasis is on particulate size and pulmonary aerodynamics. *Environmental Science & Technology* seems to be the journal that contains the majority of current reports on lead aerosols in regions as far ranging as central cities to middle Pacific Ocean air. These studies cover sources, geographical distribution, transport, meteorology, and analytical methodology. However, the only report that attempts to consolidate all the quantitative data is the Battelle report (1970). Many of the other reviews give diagrams of environmental transport similar to Battelle's pollution chain; however, they do not go much beyond a qualitative discussion of the factors influencing this transport. Within the past few years, a heavy emphasis on the fallout of particulate lead and on lead exposure via dust has developed.

#### *Lead in plants and soils*

The studies of lead in soil are almost the same as those for the atmospheric dispersion of lead aerosols. There are few studies available on the chemistry of lead within the matrix of soil structure and these are found primarily in works on plant uptake of lead. **Lead in Soils and Plants: A Literature Review** (Chemical Rubber Co. Press, Vol. 3) cites 129 references and gives extensive details of these research efforts. The bulk of the current literature seems to be in the three journals: *Environmental Science & Technology*, *Journal of Environmental Quality*, and *Environmental Pollution*. It is only recently that researchers have realized that lead is basically a surface contaminant of plants. There is a noticeable confusion in the earlier literature that can be explained by an understanding of surface lead and

the various methods used for handling, washing, and preparing samples of plant material. The emphasis of current literature is on sample preparation procedures.

#### *Human exposure to lead*

##### A. Industrial exposure

Industrial exposure is perhaps the best-documented source of lead to humans, and was historically the first source recognized and studied. Extensive studies have been conducted around smelters, battery factories, scrap reclaiming facilities, chemical plants producing lead salts, and gasoline refineries.

Generally, symposia and reviews extensively cover this field—although some tend to report individual cases, (see National Academy of Science, 1972, *Arch. Environ. Health*, 1964 and NTIS, 1970). The medical journals are particularly strong in this field, although they tend to ignore the geographical and meteorological factors contributing to exposure and the effects on plants and animals. The veterinary journals contain good reports of exposures to cows, horses, and sheep in areas where these animals are raised close to lead refineries. Several exposures have been reported, particularly in the Italian medical journals, of workers in plastics factories where lead salts are used as hardening agents; these are abstracted in the **Annotated Bibliography** (1972). Exposures have also been reported in the shipping and transportation industry, when containers of lead salts were broken, and in agriculture, when lead insecticides were inadvertently used for livestock consumption.

##### B. Air and respiratory absorption

In recent years, extensive investigations on the effect of particle size of lead aerosols on respiratory absorption have been undertaken. This work has been primarily associated with studies of urban air quality and lead gasolines. The relation of respiratory deposition versus particle size has also been extensively researched in medical and pharmacological studies where drugs were administered in aerosols. These studies may be found in the literature on asthma and emphysema. A good review of the physiological aspects of particle size in the lungs may be found in "Accumulation of Toxic Metals with Special Reference to Their Absorption, Excretion, and Biological Half-Times" (*Environ. Physiol. Biochem.*, 1973). *Science* has recently published several papers on the particle size of lead in air, and *Environmental Science & Technology* frequently has papers on this topic.

Although research on particle size has been active since at least the early 1950's, very little of this information has been included in the symposia and review articles. Of importance is the fact that there is no reported information on absorption in children or immature animals, nor even of the normal respiratory dynamics of children.

##### C. Ingestion of lead

Surprisingly little information has been published on the lead content of specific food items, although there is ample information on average intakes in the medical literature. The literature does indicate that, for practical purposes, most of the lead contamination found in food is added in processing and packaging. Thus, the levels found in supermarket items in New York City (*Health Phys.*, 1971) may be considered typical, since food processing and packaging are relatively homogeneous industries, and most items get shipped throughout the country. The **Annotated Bibliography** (1972) has many abstracts on lead in food, but most of these discuss how the lead is added during food processing, or from food containers, paper wrapping, and cooking utensils.

In contrast, the problem of pica in children (DHEW, 1973) and in puppies (*Clin. Toxicol.*, 1973) has been extensively documented in the medical literature. In addition, the ingestion of lead by farm animals, particularly in regions adjacent to lead smelters, has been extensively studied. These animal studies are well-supported in the symposia, especially the EPA's International Symposium at Amsterdam (European Communities, 1973). The exposure of farm animals to lead products is summarized in a veterinary symposium (*Clin. Toxicol.*, 1973), where it is indicated



that cows are particularly prone to lead's toxic effects because of their predilection for non-food items such as crankcase oil and metal scraps.

#### *Deposition and storage of lead in tissues*

Knowledge of lead in tissues has progressed beyond the general principle that lead is stored in bone and transported in blood, and that the soft tissues are in equilibrium with the blood. The information found in the symposia ranges from a listing of blood concentrations only, to rather specific details on many tissues (NTIS, 1970). The **Annotated Bibliography** (1972) has a large number of abstracts on lead in tissues from teeth to body fluids.

The medical literature is primarily concerned with blood-lead levels, although reports on other tissues such as bone, brain, and hair occasionally occur. Current medical and environmental sciences literature indicates an interest in the use of hair as a biopsy material. Also, the Japanese journals in the 1950's carried many reports of studies on lead levels in hair. Placental transfer and the differences between organic and inorganic lead compounds have also been studied (**Annotated Bibliography**, 1972 and NTIS, 1970).

Current literature in the environmental journals appears to emphasize the effects of lead storage in the kidney and its age dependency and, in addition, the mechanisms by which particulate lead is assimilated and stored in the lung. Veterinary literature is less active in this field, but published reports usually contain measurements on a wide variety of tissues from clinically ill and sacrificed animals. There seems to be a need for some standardized procedures for handling these issues and reporting results so that more confidence can be placed in comparing the work of different investigators. For example, a very elementary problem arises in the use of hair as a biopsy material. Some investigators use clippings from barbershops, while others use total hair samples clipped at the scalp, and still others use only an inch or two proximal to the scalp. The literature does contain

reports that detail differences in the lead content of hair as a result of its location on the body, hair color, race, growth rate, and age of the donor.

#### *Effects of lead on body chemistry*

The studies on the biochemistry of lead have been concerned with the inhibition by lead of the enzymes responsible for red blood cell formation. It should be noted that, of the common experimental animals, these disturbances in enzyme levels occur only in humans and rabbits (*Clin. Toxicol.*, 1973). The blood and urine enzyme levels are well-established diagnostic tools used clinically for diagnosing lead cases. Several years ago the reports on the enzyme studies were confined to the medical literature, but many of these reports are currently appearing in the environmental literature, particularly in *Archives of Environmental Health*. The review articles all give schematic representation of hemoglobin synthesis, and specifically discuss those enzymes inhibited by lead. The current literature is concerned with factors that influence the rate and extent of this inhibition.

#### **Additional topics**

##### *Lead metabolism and kinetics*

The quantitative study of lead kinetics is relatively new because of the difficulty in controlling lead exposure. The recent availability of methods for handling the stable isotopes of lead has renewed interest in these studies. Several research efforts are currently in progress, and initial reports are beginning to appear (*Science*, 1973 and *Environ. Health Perspectives*, 1974). The Battelle review (1970) and an international task group's report (*Environ. Physiol. Biochem.*, 1973) give good summaries of the earlier work.

##### *Species-specific effects*

Since lead toxicity in agricultural animals is an important problem to farmers and ranchers, the effects of lead on horses,

cows, and sheep are well documented in veterinary textbooks. Many dose-response studies have been reported, particularly in the European literature. Because of these studies, species-specific effects became apparent; these are adequately summarized for all common animals in a veterinary symposium (*Clin. Toxicol.*, 1973). Although lead is toxic to animals, the mechanism of that toxicity varies widely among species. Only the rabbit of the common animals is close to man in toxic manifestations. It is somewhat disconcerting to see the results of metabolic experiments on lead using adult rats extrapolated to man without qualification, since these animals can tolerate about four times more lead per kilogram than humans, and the toxic manifestations are different.

#### Treatment and clinical toxicity

The medical and veterinary literature has extensive references to the treatment and clinical manifestations of lead toxicity. Basically there are three types of drugs currently known to be effective in treating lead toxicity, but their names or acronyms appear in a multitude of generic and abbreviated forms. As an aid in a literature search by title, it is helpful to be familiar with the following more commonly used varieties of drug names, acronyms, and trade names:

- calcium-ethylenediaminetetraacetic acid (Ca-EDTA)—also known as edetate, calcium-edetate, sodium calcium edetate, edathmil calcium disodium, calcium-ethylenediaminetetraacetate, calcium disodium versenate, Versenate, EDTA, or similar word combinations.
- British anti-lewisite (BAL), also known as 2,3-dimercaptopropanol and Dimercaprol
- Penicillamine (PCA), also known as penicillinase, Cuprimine, and Neutrapen.

A good source for these articles is the medical departments of the pharmaceutical companies that market the drugs. Most hospital libraries have **Index Medicus**, which gives an almost complete abstracting and subject cross-reference of the medical literature. A better but lesser known abstracting service is the National Library of Medicine's **Selected References on Environmental Quality as it Relates to Health**. Toxicology, occupational health, and environmental health journals also publish articles on the clinical effects.

Articles on problems in differential diagnosis are not common. They characteristically appear in the basic science literature, are widely scattered, and are often presented as incidental observations in reports on other topics. Other heavy metals, fluorides, insecticides, household chemicals, and ornamental plants have caused diagnostic problems. In addition to the ingestion of subclinical levels of lead, these other agents may be ingested, especially by children, and then may be responsible for some of the confusion in diagnostic criteria—particularly for blood-lead values. The Kettering symposium (*Arch. Environ. Health*, 1964) contains a good discussion of diagnostic problems, and the veterinary literature discusses differential diagnosis with respect to other agricultural chemicals.

#### Seasonal and geographic variations

The fact that non-occupational lead toxicity is a summertime disease has long been recognized in the medical literature. Recent interest in the seasonal variation of atmospheric lead has renewed interest in this field of lead research (National Academy of Sciences, 1972); however, this interest has only illustrated and has not elucidated the complexity of the problem. For example, urban air-lead levels are highest in winter, whereas clinical toxicity is a summertime phenomenon. Animals seem to show the same seasonal pattern. For example, urban dogs have been shown to have the same exposure and response as children (*Clin. Toxicol.*, 1973) and rural cows in Iowa have also shown the same seasonal pattern even though there is no known seasonal variation in exposure. The medical literature also reports a seasonal variation in persons who ingest lead from moonshine whiskey, even though there are no apparent seasonal variations in consumption.

It has also long been recognized in the medical literature that lead toxicity, in general, seems to be geographically confined to the eastern half of the U.S. There is still some question as to whether this geographical effect is real or due to differences in medical awareness of the disease. The epidemiological studies of blood-lead levels in children found in the medical literature (and discussed under the Environmental transport and occurrence section of this paper) indicate that there is little geographical variation in the blood-lead levels of children in urban areas. The air pollution literature indicates that there is seasonal variation in mortality with high heat and humidity being associated with increased mortality (*Environ. Res.*, 1971).

The studies of seasonal and geographical variations in humans seem to be confined to large urban areas of the U.S. and Japan. Some experiments have been reported in the environmental literature investigating the effects of temperature extremes and dehydration on lead toxicity. However, extreme conditions were used, massive doses of lead given, and rats were used as the experimental animals. Thus, it is unlikely that these results are applicable to the observed seasonal and geographic occurrences in humans. This field of research seems to be one that has not been extensively investigated, and is one area that must be clarified before exposure criteria can be well established.

#### Synergism and potentiation of the toxicity

Studies of synergism and altered susceptibility have been reported for many years (**Annotated Bibliography**, 1972). Most of the material on differential diagnosis should be consulted by those interested in synergism. The literature on lead metabolism discusses those agents that alter the absorption and transport of lead. For instance, respiratory acidosis, renal disease, systemic bacterial infections, and hyperparathyroidism are all known to cause the release to the bloodstream of the lead stored in bones (*Arch. Environ. Health*, 1964). The works discussed in the previous section on seasonal variation, in which exposures and effects seem inversely related, strongly suggest some as yet unknown meteorological synergistic factors. One review of lead toxicity (*Environ. Health Perspectives*, 1972) extensively discusses the medical aspects of altered susceptibility resulting from dietary deficiencies and genetic factors.

It is certainly a reasonable hypothesis that many as yet uninvestigated environmental pollutants could affect lead metabolism in ways similar to known disease states. Such agents could be responsible for the observed seasonal effects, and the fact that toxicity is not closely associated with lead exposure. Before environmental standards for lead exposure can be unequivocally established, these factors must be extensively studied and those factors found to be synergistic and environmentally important must be integrated into lead surveillance projects.

#### Additional reading

"Impact on Man of Environmental Contamination Caused by Lead." Colorado State University. National Technical Information Service, PB-223-622. (169 pp).

"Environmental Pollution by Lead and other Metals." University of Illinois. National Technical Information Service, PB-222-824. (438 pp).

"The Environmental Impact of Lead." U.S. Environmental Protection Agency, Health Effects Research Laboratory, Cincinnati, Ohio. To be published. (720 pp).



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# Interdisciplinary research in the university setting

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Problems of interdisciplinary research in the university setting are difficult to identify and analyze since most faculty members consider these coordinated efforts an art rather than a science. Rarely is this topic discussed in publications, and few empirical studies are published anywhere. The practice of interdisciplinary research is clouded by myths, half-truths, and misconceptions. Those practitioners finding the effort rewarding continue to develop and promote the practice; those having unsatisfactory first experiences grow bitter and usually become harsh critics.

At the University of Washington, a group of professors, administrators, and graduate students is conducting a 2-yr investigation into the "Assessment and Experiment With Management of Large-Scale Interdisciplinary Research Projects," as part of the continuing research management improvement effort. This research is one of nine related projects supported by the National Science Foundation. The project is only at the half-way mark and final results will not be published until late 1976; therefore, the observations reported in this paper are subjective.

## What is it?

There is disagreement on the use of the term "interdisciplinary research" and the form that it should take. In the university setting the *ideal* interdisciplinary effort seems to be made by a number of faculty members from various disciplines, pooling and integrating their knowledge and resources to focus on a problem that an individual working alone could not possibly address effectively. In practice, this ideal is seldom reached, and what usually occurs is the formation of one of several alternative forms:

- Multidisciplinary group. Here, the problem is divided and the separate disciplinary roles are defined independently of the others in the proposal. When the effort is funded, each member conducts his/her research independently, and the research results are integrated by the staples of the final report.
- Cross or bidisciplinary group. Two faculty members, each from separate but closely related disciplines collaborate on a study.
- Interdisciplinary staff/students group. A single faculty member collects students or staff from separate disciplines and directs them in a research activity.
- Multidisciplinary individual. A single individual undertakes a course of study in several disciplines or, by informal education, obtains knowledge of several disciplines. This individual then applies the combination of skills to a research problem.

From these examples it is clear that the common feature of these variant forms is the application of several disciplines to

a single problem; what differs from form to form are the organizational and interpersonal relations. Thus, a principal feature of interdisciplinary research is not necessarily profound scientific development, but an improvement in *human relations* to overcome the intolerance, bigotry, and barriers not only among individuals, but within and among disciplines.

## The problems

Almost any interdisciplinary organization and management problem can be traced to a people problem. Common issues encountered in discussions of interdisciplinary research usually focus on the problems of recruitment, resources, and quality of the research. This paper will focus on the recruitment and resource issues, since research quality currently seems to be measured by the quality of the researchers rather than their product.

The quality of interdisciplinary research is often questioned because of the applied nature of this research, the need to envelop concepts from the whole yet not necessarily the frontier of each discipline involved, and the involvement of people for their breadth as well as depth of knowledge. Countering such arguments is the growing number of societal problems that need to be addressed and cannot be solved by fragmented individual research. Such problems seem only to yield to interdisciplinary analysis and some mechanism needs to be found to stimulate such research in the university setting.

Faculty members have been trained and selected for their ability to conduct individual research and for their individual excellence, not for their ability to participate in a team effort. They become critics of their peers, stimulating each other to heights of excellence and personal achievement. When a faculty person, especially a younger member, undertakes interdisciplinary research there is a high risk that his or her peers will not recognize this pursuit as a significant activity since it runs counter to the traditional primary goals of achieving individual excellence. Additionally, in academic settings where resources are scarce, the interdisciplinary activity usually grows at the expense of existing units. This reallocation of scarce resources creates competitive strains.

Finally, from observations of interdisciplinary teams, one recurring feature has been found to be a highly unstable and unproductive initial development phase that lasts several years. This initial inertia can be overcome only through extensive investment of time and resources by those participating in the interdisciplinary process. In summary, the development of in-

the problems—both personnel and financial—and the rewards are clearly defined

"Interdisciplinary research is too much trouble . . . that's the last time I Get Involved!"

terdisciplinary research in the university setting faces severe human relations problems since the process itself creates change and threatens existing units. New reward systems must be created, new units must challenge existing units, and new coalitions need to be formed.

#### People-problem solutions

One of the few articles in the scientific literature that speaks to the interdisciplinary research problem in terms of people problems is Holling and Chambers paper "Resource Science, The Nurturing of an Infant" (*BioScience*, 1973). The roles that must be taken by the participants in such a coordinated research effort are presented. Mar and Newell (RANN Report, 1973) report that one of the critical forces in such activities is communication. They report that each discipline has developed such a sophisticated jargon that a novice cannot understand the nomenclature much less the concepts. When scientists from several disciplines attempt to discuss a potential interdisciplinary research topic it may require a year for individuals from two different disciplines to gain sufficient command of each other's nomenclature to hold a constructive dialogue.

Constructive communication requires a long period of interchange that seems scientifically unproductive. Individuals that master an encounter with one discipline seem more effective in the next encounter with another discipline; a process of facilitation seems to occur. There seems to be an increase in tolerance and patience as more interdisciplinary experience is obtained. On the other hand, individuals who are committed to academic specialization have grave difficulties participating in interdisciplinary efforts.

Disciplines themselves may inherently have some intolerance of other disciplines; in fact, segments within the same discipline may claim superiority, excellence, or intellectual distinction over others. Examples that readily come to mind are the disdain of scientists for engineers, or mathematicians for physicists, or pure scientists for applied scientists—a disdain perpetuated by many faculty members unconsciously if not consciously.

#### Experience helps

A preliminary analysis of our survey of interdisciplinary efforts around the country indicates that there are several actions that can be taken to reduce the human relations problems. These can be categorized into two basic philosophies. The first category is the *pool* concept where faculty members from many disciplines belong to a department, college, study group, center or institute and occasionally participate in interdisciplinary research.

There are departments and colleges that have interdisciplinary faculty by choice in an attempt to overcome institutional barriers. Centers and institutes are less formal organizational forms. The pool concept creates a mixed faculty that leads to successful interdisciplinary encounters, has some degree of favorable personal interaction, and a higher degree of tolerance for other views. These faculty members will tend to form teams to respond to proposals. Since they have prior experience with other disciplines (and the few faculty in the team who lack this experience are influenced by those who do), communication problems are minimized. Members of pools, in addition to interdisciplinary research, also pursue individual research efforts.

Since many of the interdisciplinary issues relate to reward and cognitive issues, formal units will promote and foster interdisciplinary activities more than informal units. On the other hand, a formal unit can become inbred and as inflexible as any disciplinary unit and lose its true interdisciplinary flavor.

While the pool concept does reduce communication problems, it does not eliminate human-relation problems. Even in departments or colleges that have faculty from many disciplines, personal animosities still exist. The pool organization does not produce a stable team, but provides an effective organization whereby different talent can be assembled rapidly to address a problem effectively.

The other approach to interdisciplinary research is the careful nurturing of a research team through the communication phase into a productive research unit. This approach has a high probability of failure unless strong personal relationships can be established among the team members. Most successful teams are not designed but happen either by chance interaction of a compatible set of individuals or by an extensive flow of individuals through the team until some "magic" combination is achieved. It is not unusual for 50 or more individuals to flow through a group before a handful of individuals "settle out" and begin the integration process.

The nurturing process usually involves individuals that have not previously worked together; this type of group usually forms as a result of:

- A charismatic leader: He/she has the ability to attract and persuade others to join.
- Senior leader: Team members join because they feel they can gain prestige or knowledge from a recognized leader.



"What does he know about it? . . . He's only an engineer!"

I know one faculty member who can work with me . . .

But no one else can!

- A common enemy: A faculty faces common problems such as lack of recognition or resources, and feels that a group can solve these dilemmas.

- A common subject or client: Needs of client or subject overwhelm personal differences and a group coalesces to focus on a common problem.

In each of these alternatives, a driving force exists that can temporarily hold a team together until the communication and nurtural reinforcements develop to form a permanent bond for the group.

In the case of a strong leader, a group may result from the force of submission rather than positive interdisciplinary synergism. Thus experiences that involve graduate students, staff, or consultants result in faster group cohesion, but do not guarantee interdisciplinary group productivity. The common enemy or target approach seems to be the most productive since a common concern can take dominance over individual differences. In all cases, whether the pooling or nurturing concept is used to form interdisciplinary teams, the start-up costs are extremely large and the maintenance costs are not trivial.

A team of three individuals from three different disciplines will require at least one year and probably two or more to reach the stage where effective intellectual communication occurs. In the case of a nurtured group, the actual cost, if fully compensated, might go as high as \$25 000–\$50 000. And this amount covers only the development of team cohesion and concept, not the initiation of research. While team development under the pool concept initially appears to be less costly—as individuals can prepare proposals and develop research concepts in a short time—it must be remembered that at some point each team member has gone through the same costly learning experience that the nurtured team member has. The difference between the two concepts seems to be that each time an individual participates fully in an interdisciplinary effort, the easier the effort becomes and the more rapidly actual research may be initiated. Yet, even a pooled interdisciplinary effort can cost many tens of thousands of dollars if personalities or values conflict and cannot be resolved.

#### Money matters

These communication costs are an underlying factor in the

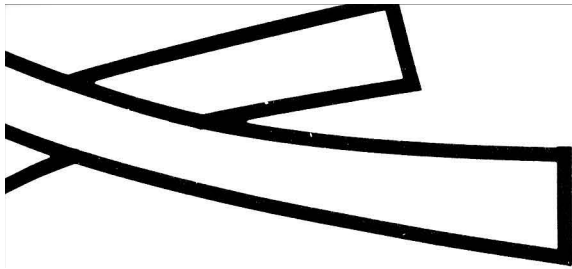
pattern of interdisciplinary team development at various universities. Usually, once funding is obtained from an agency, a significant fraction of the funds can be diverted into stabilization and team development activities. When funding agencies lack experience in selection of interdisciplinary research teams, they are dismayed to find their funded teams disintegrating or changing over the grant period as communication and human-relation problems are encountered. When teams are improperly formed during the proposal stage, the teams may disintegrate after funding is received because members cannot agree on division of the funds or allocation of tasks. A funding agency takes greater risk funding a "nurtured" group than a "pooled" team. The pool team has prior experience and sufficient backup members to supply added human resources. When a nurtured group loses a member, the entire effort can fail.

Thus, universities provide seed monies that permit existing grant funds to be diverted to team development, or in other ways encourage interdisciplinary research; in effect, the universities "pay the dues" of the initial team development costs (\$25 000–\$50 000). At universities where resources are not available and faculty see no merit in devoting the needed monetary level of effort, interdisciplinary research is difficult to establish. Funding agencies that seek to encourage coordinated research must learn to accept these costs by funding planning or development grants. These grants would, in the long run, be less costly than the funding of efforts that fail to achieve interdisciplinary status. For every \$100 000 of interdisciplinary grants that have failed, two to four new groups could have been created.

At many universities, money is not an effective incentive. The established researcher is usually overcommitted and, furthermore, many universities' rules limit the funds a faculty member can receive. The "release time concept," common in many universities, only permits a faculty member to substitute one paid activity for another; it does not add cash-in-hand. In institutions in which faculty members have heavy teaching loads and very few research opportunities, release time that reduces teaching loads can be a very attractive incentive. Unfortunately, many of these faculty members have little research experience of any type and this lack of experience must be overcome.

There appear to be several other resources that are more valuable to faculty than money. These resources vary from institution to institution, but at least one of the following resources could be an incentive that would attract faculty members to participate in an interdisciplinary effort. In institutions where research is common, the incentive must take the form of space or services, since existing research provides the stimulant, funds, and other rewards. The availability of laboratory, office, and working space is a limited commodity on most campuses. A team leader that offers space can often recruit faculty when all else fails.

One of the most attractive services that can be offered to faculty is the provision of a test population or subject. A wise



team leader, funding agency, or university administrator can stimulate team formation by establishing resources for maintenance of the subject of research. For example, a clinic or animal colony has major appeal in medical studies, a lake or similar ecosystem has major appeal for environmental studies, and a major laboratory facility has appeal to scientists. Another form of incentive seems to be the availability of scientific and administrative staff to conduct or support research; but this addition of staff can be a dilution of effort rather than a multiplier for interaction.

In the early stages of group development, the timing of resource availability is almost as important as the type and amount of incentive provided. Normally, scientific curiosity provides sufficient cohesive force for the proposal development and initial group development. If there are research novices on the team, a debate can occur between those that feel that excellence and thoroughness of scientific reasoning must be highly developed prior to approaching a funding agency and those that feel that a balance must be achieved between funding agency program plans and preferred research by the team. If those demanding excellence prevail, the cost of team development will be extremely high and the demoralizing impact of initial funding agency rejection will be especially destructive.

At the proposal submission stage, the teams need monetary incentives that are limited to marketing and travel activities. Such assistance will increase the groups' perception of the funding agency's needs, increase the probability that their concepts are well-received, and soften the impact of agency rejections. It is surprising how little knowledge of the research funding process most faculty members have.

Funds that are provided prior to the formation of a group, or prior to the identification of common goals do not seem to be effective in assuring continued group development. The provision of funds when major crises face the developing team is more significant than initial funding when the team is gathering momentum or in productive stages.

### Summation

While the observations presented here are speculative and subjective, a major thrust of this project on the management of interdisciplinary research is to provide quantitative insight. A three-pronged attack to identify issues and experiences of university administrators, center and institute directors, and interdisciplinary project teams at many universities across the nation is under way. Data are being collected from extensive on-site interviews and formal questionnaires and will be published early next year. Based on a preliminary assessment of these data we suggest the following hypotheses:

- University administrators generally do not differentiate between the costs or problems of interdisciplinary research projects and disciplinary research efforts. Some faculties are expected to develop interdisciplinary efforts with no more help than that provided disciplinary efforts; much of this cost is passed on to the funding agency in terms of less productive research in the first few years.
- While a center or institute can provide an umbrella and a voice for faculty wishing to pursue interdisciplinary research, experience has shown that such units work hard to obtain a firm base of financial support. Once such funding is achieved the interdisciplinary zeal slowly fades because the participating

faculty work hard to exclude new members to avoid further division of existing resources.

- Management strategies affect interdisciplinary research team performance. No one strategy has been able to create the commitment and cohesiveness necessary in a successful team. But the more types of integrating mechanisms a group uses (such as workshops, seminars, continual documentation) the more interdisciplinary it becomes.

- Since faculty members tend to concentrate on the frontiers of their disciplines, and interdisciplinary research requires the whole breadth of knowledge in a discipline, it may not be necessary to have a team solely comprised of basic researchers. A balance of application and pure research will always be necessary.

- Quality control presents a challenge for any interdisciplinary research on campuses as peer review is difficult to develop.

Given the lack of published information concerning interdisciplinary research, readers of *Environmental Science & Technology* are invited to complete a questionnaire that can be obtained from the authors. These responses will be integrated with the data obtained in the NSF-sponsored studies, which will provide insights into future interdisciplinary studies.

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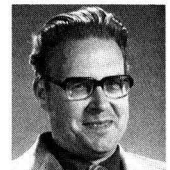
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# . . .Reducing coke plant effluent

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Fifty years ago, the production of coke from by-product ovens began to surpass coke production from beehive ovens. The by-product process became predominant because it possessed two significant advantages over beehive coking: first, the fact that by-product processing allowed considerable chemical recovery; and second, that by-product processing markedly reduced air pollution problems associated with coking.

The last decade, however, has brought a changed perspective. Heightened environmental awareness has called attention to substantial air pollution problems that remain a part of the by-product process. Similarly, although oven-coke production has remained stable at 60–70 million tons per year, chemical recovery has grown increasingly less advantageous, with the value of coal chemicals now representing only about 10% of total product value. At the same time that these changes have taken place, increasing attention has been focused on another principal difference between by-product and beehive coking, namely, the introduction of significant water pollution problems that are a direct consequence of the gas processing.

Pursuant to the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500), coke plant effluent limitations have been imposed by the Environmental Protection Agency (*Federal Register*, Vol. 39, No. 126, June 28, 1974). Coke plant wastewaters are typically as saline as seawater, and contain a broad range of organics. Limitations are set for oil and grease, suspended solids, pH, and sulfides, but the guidelines are aimed principally at the control of ammonia, cyanide, and phenolics. The guidelines call for more than 90% reduction of these pollutants from their former levels in typical untreated process waters by 1977. Further control by 1983 is expected to reduce discharges of the three by more than 99% (Table 1).

## Coke plant wastewater sources

By-product coke plants vary widely in size, extent and type of by-product recovery, and wastewater practices. Wastewaters in coking originate from three principal sources: coal moisture, water of decomposition, and process waters added during gas treatment and by-product recovery. The process waters are the largest fraction of the total wastewaters and typically account for 60–85% of the total flow, which may range from 120–310 gal/ton depending on the level of process water recycle. Typical gas processing and recovery steps are shown in Figure 1, which indicates the six categories of wastes normally identified:

- tar still wastewater (1)
- waste ammonia liquor (WAL) from the primary cooler (2)
- ammonia absorber and crystallizer blowdown (3)
- final cooler wastewater blowdown (4)
- light oil (benzol) plant wastewater (5)
- gas desulfurizer and cyanide stripper wastewater (6)

Loose or tight recycle is a measure of the flow reduction achieved through recycle and process modification in the final cooler and the benzol plant. Mass emissions are essentially the

TABLE 1  
Effluent limitations for selected coke plant pollutants  
(pounds per million pounds of coke)

Pollutant	Typical raw wastewaters	BPCTCA (1977)	BATEA (1983) <sup>a</sup>
Ammonia	914	91.2	4.2
Cyanide	120	21.9	0.1
Phenol	262	1.5	0.2
Average percent removal	0.0%	91.2%	99.7%

<sup>a</sup> These limitations may change if Congress follows recent recommendations of the National Commission on Water Quality.

same for both configurations, with the exception of some loss of pollutants for tight recycle because of by-product contamination, volatilization to the atmosphere in open cooling towers, and development of corrosion products in the coke oven gas distribution system.

One way to characterize the environmental impact of these wastewater streams is to construct an overall mass balance for emissions to the air, water, and the land. The mass balance must be drawn around the principal parts of the plant: coke ovens, quench towers for the incandescent coke, by-product plant, and an associated plant to treat the wastewaters. Figure 2 shows the principal plant input consisting of coal, and the main outputs of coke, coal chemicals, and coke oven gas. The mass emissions balance must include air emissions from the open cooling tower and the quench tower in the form of volatiles and particulate matter. Water emissions may be adequately represented by wastewater loads of ammonia, cyanide, and phenol. To control the wastewater effluents to the degree required by current regulations an energy plant must be considered as part of the coke plant system.

## Energy requirements for wwt

The energy plant consists of a coal-fired power plant that raises steam and generates electricity for the wastewater treatment (wwt) plant. The power plant also produces emissions, even though the plant is configured to meet applicable air and water regulations. Particulate matter, sulfur dioxide, nitrogen oxides, and waste heat are emitted to the air. Waste heat also goes to the water, while the land receives ash and SO<sub>2</sub> scrubber sludge from the power plant, as well as demineralization sludge from boiler water treatment (Figure 3).

Here, an interesting situation arises. It is apparent that as one problem is solved—the wastewater effluent problem from the

FIGURE 1

Coke plant waste processing/recovery

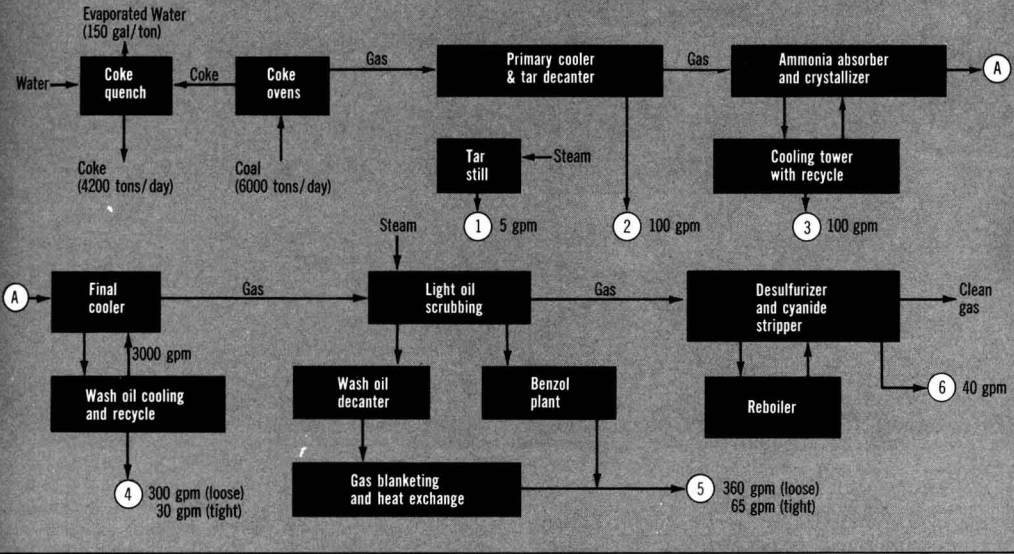


FIGURE 2

Coke plant schematic

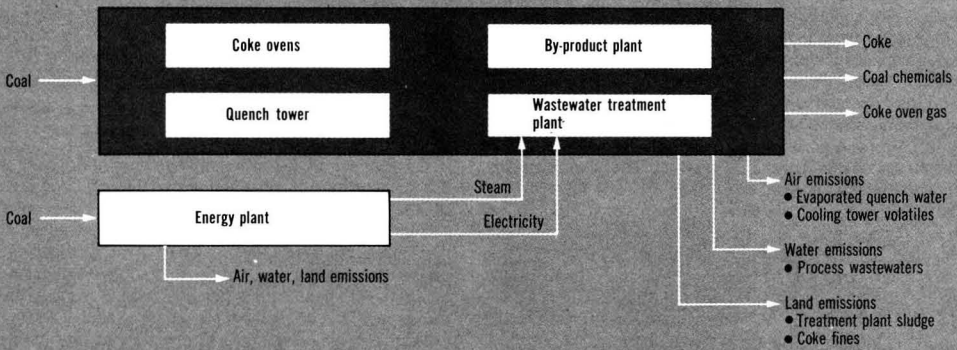


FIGURE 3

Daily inventory for selected pollutants from a 4200-ton coke plant

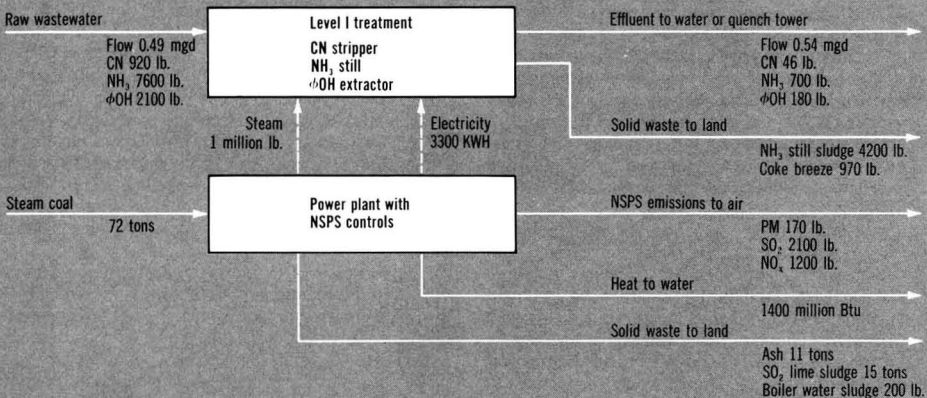
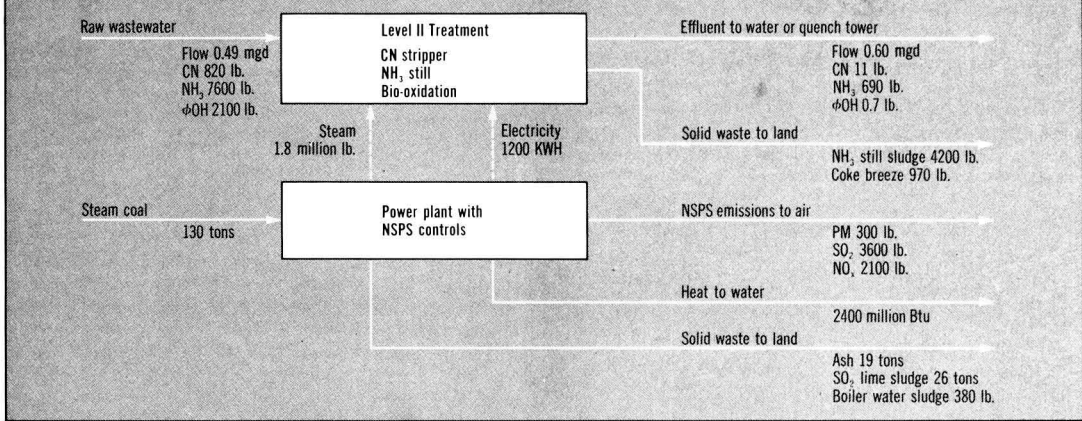




FIGURE 4

Daily inventory for selected pollutants from a 4200-ton coke plant



coke plant—other emissions are created, namely, effluents produced from generation of required process steam and electricity for the treatment system. Furthermore, the amount of process energy required—and the amount of secondary effluents produced—increase dramatically as the level of wastewater treatment becomes more stringent.

Thus, several questions are posed. Is environmental control being implemented at cross purposes? What is the net environmental impact for disposal of all effluents? How can an optimum level of wastewater treatment be defined, a level that achieves the maximum environmental improvement and takes into account all effects? To answer these questions it is necessary to perform a careful environmental assessment of the coking operation, including an examination of alternate strategies for handling the wastewaters.

Total effluents for the wastewater treatment strategies are shown in Figures 4 and 5 for a hypothetical coke plant modeled for this study. The treatment strategies are composed of unit processes and recovery operations that have been commercially demonstrated. With a daily coal charge of 6000 tons and a daily furnace coke production of 4200 tons, such a coke plant would be among the largest 25 plants in the country.

Level I treatment is wholly a physical-chemical system that uses a method for cyanide stripping based on existing technology developed by Bethlehem Steel Corporation—ammonia removal with a conventional still—and phenol extraction based on existing technology developed by Jones & Laughlin Steel Corporation. Level II is a higher level of treatment, combining physical-chemical operations with biological waste treatment. The biological plant is similar to an existing facility at Bethlehem Steel and is designed to reduce the carbonaceous oxygen demand, with performance primarily set for phenolics reduction. These treatment systems do not precisely correspond to treatment levels designed to meet current EPA BPCTCA or BATEA limits. However, Level I meets BPCTCA guidelines for cyanide and ammonia; Level II meets all BPCTCA guidelines and the BATEA guideline for phenol.

The different control strategies each result in pollutant emissions to the air, water, and land. Air emissions originate from the coke quench tower, from the open cooling towers, and from the power plant supplying electricity and steam to the treatment plant process units. Water effluents arise from coke plant wastewaters, from blast furnace wastewaters that account for pollutants transferred by wastewater quenching, and from power plant waste heat discharges. Land contamination originates at the power plant, the quench tower, the boiler water treatment

plant, the coke plant ammonia still, and the coke plant's biological treatment facility.

An inventory of all principal pollutants emitted to air, water, and land for each of the selected control strategies has been compiled. Emissions estimates were generated for eight pollutants emitted to the air, six pollutants to the water, and five pollutants to the land. By itself, such an accounting of residuals shows the relative complexity of the problem. However, in order to select an overall best strategy for the environment as a whole, an aggregate summation of these different residuals and their effects must be attempted.

**Cross-media analysis**

Comparison of the complete inventory of emissions with the original wastewater loads shows that the reduction of emissions of ammonia, cyanide, and phenol to the water involves the generation and discharge of many other pollutants and treatment residuals to the air and land. To obtain a more unified perspective on the mass emissions, it is useful to convert all the emissions to a dimensionless index that sums their individual effects. The mass emissions are first expressed on a relative basis, i.e., each pollutant emission is scaled from zero to one, based on the maximum uncontrolled emission for each pollutant. The normalized mass emissions for all pollutants are then assigned weighting factors chosen to reflect the relative impact of each pollutant on a given medium.

These weighting factors may be site-specific. The authors' choices for this study were based on consideration of several sets of national air and water quality criteria. The weighted sum of all the pollutants to the air, water, and land is the Environmental Degradation Index (EDI) for each control strategy. Reiquam, Dee, and Choi at the Battelle Memorial Institute developed a technique for using this index, termed Cross-Media Analysis (*ES&T*, February 1975 p 118). The authors have modified and extended this methodology. Large values of EDI are interpreted as undesirable. The relative change in EDI compared to a base case of no control shows the net improvement or degradation of the environment for a chosen strategy relative to the no control case.

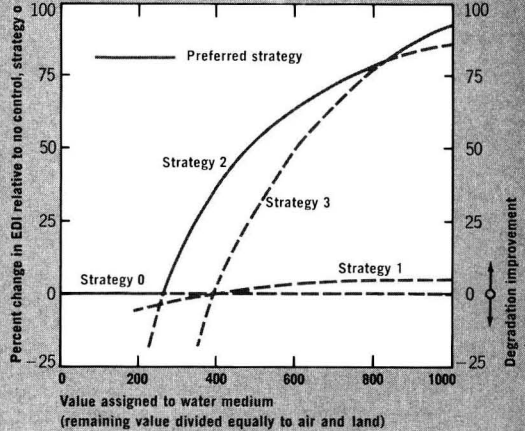
The change in EDI for three control strategies for coke plant wastewater management are shown in Figure 5. This display, termed a preference plot, shows the net environmental effectiveness of the control strategies as a function of the total value assigned to the water medium as a depository for wastes. The preference plot shows that the dominant control strategy, i.e., the strategy with the greatest positive improvement over the



FIGURE 5

Preference plot for coke plant wastewater environmental control

Strategy	Recycle	Wastewater treatment	Effluent discharge
0	Loose	None	To watercourse
1	Tight	None	To watercourse
2	Tight	Level I	To watercourse
3	Tight	Level II	To watercourse



base-line no control case, varies with the weight assigned to the water medium. At very low water medium values, the least amount of control is preferred; for very high water medium values, the greatest degree of control is preferred.

Hence, one of the principal judgments involved in the analysis is the assignment of relative values for the media. More specifically, if 1000 points are to be assigned collectively to the three media, how should the assignment be made? The results displayed in Figure 5 show that assignment to the water medium of 250 to 850 of a possible 1000 points results in a preference for an intermediate degree of wastewater treatment. For this example, media points not assigned to water are divided equally between air and land. A complete analysis requires the generation of many preference plots in order to check the sensitivity of the change of EDI to the important variables in the analysis.

Results of the analysis

It is useful to view the coke plant problem from the standpoint of three practices—type of quench water, level of process water recycle, and level of treatment selected for wastewaters. The cross-media analysis leads to the following observations:

- Quenching with coke plant effluents, regardless of their level of treatment, is normally the preferred practice for greatest net improvement of the environment. This practice is preferred over discharge of that effluent (at the same level of treatment) to a watercourse.
- Tight recycle of cooling waters rather than loose recycle is normally preferred for the greatest net environmental improvement.
- For values of media weights that appear most reasonable, an intermediate degree of wastewater treatment (Level I) is preferred practice over either no treatment or Level II treatment, if the greatest net environmental improvement is to be achieved.
- A high degree of wastewater treatment (Level II) appears to be preferred only as a single-medium solution; i.e., if the water medium is viewed as dominant and is valued out of proportion to air and land media. Similarly, a low degree of wastewater treatment appears to be an environmental strategy in which water as a medium is relatively disregarded.

These results suggest that the current EPA effluent standards for by-product coke plants, in particular the BATEA (1983) limits, are too stringent to maximize the net environmental improvement that can result from the treatment and disposal of coke plant wastewaters. The results of this study also clearly support the contention that levels of environmental control must be

considered very carefully if maximum improvement of the environment is to take place. A rational emphasis on net improvement of the environment, not an emphasis on single-medium regulations and solutions, appears to be the current environmental imperative.

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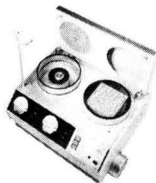
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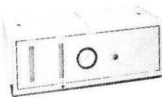
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# CURRENT RESEARCH

## Evaluation of Candidate Solids for High-Temperature Desulfurization of Low-Btu Gases

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■ High-temperature processes for desulfurization of low-Btu gases are receiving increased attention. In this study, results of thermodynamic screening of the high-temperature desulfurization potential of 28 solids, primarily metal oxides, are reported. By use of the free energy minimization method, equilibrium sulfur removal and solid compound stability were determined at temperatures to 1500 °C. Eleven candidate solids based upon the metals Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu, and W show thermodynamic feasibility for high-temperature desulfurization of low-Btu gas.

Commercial processes for the removal of H<sub>2</sub>S from gases (1) involve wet scrubbing and, consequently, operate near 250 °F. High-temperature H<sub>2</sub>S removal capability is needed if low-Btu coal gasification is to be a viable alternative to oil imports.

The reactivity of certain metal oxides with H<sub>2</sub>S has long been known. The Appleby-Frodingham process (2) utilized ferric oxide at 400 °C for coke oven gas desulfurization. ZnO at 400 °C is used to desulfurize hydrocarbon feedstock for ammonia synthesis (3). Currently, the use of limestone and dolomite for high-temperature desulfurization is being studied (4, 5).

The literature contains these and numerous other reports of reaction between H<sub>2</sub>S and metal oxides. In this study, a systematic thermodynamic screening, using the method of free energy minimization, was performed to determine which inorganic solids have desulfurization potential and to define the limits of the potential application.

### High-Temperature Desulfurization Criteria

Generically, the process of low-Btu coal gasification can be represented by the combination of coal, air, and steam to produce gaseous products rich in CO, H<sub>2</sub>, and N<sub>2</sub> with smaller quantities of steam and CO<sub>2</sub>. Sulfur in the coal will be converted predominantly to H<sub>2</sub>S. In a high-temperature desulfurization process the gasifier product will contact the solid reactant with which the sulfur species will react to form solid sulfur compounds.

Thermodynamic criteria have been established with respect to fractional desulfurization and solid stability. High fractional desulfurization is an obvious requirement. For this general study, we have taken 95% equilibrium desulfurization to be the minimum acceptable although the exact requirement will depend upon turbine specifications, coal composition, and local environmental regulations.

The stability criterion ensures that unreacted solid is stable at the conditions of interest. For example, in a low-Btu gas atmosphere, lead oxide will be reduced to metallic lead, whose melting point (327 °C) is too low to be of interest. Conse-

quently, all oxides subject to reduction to low-melting metals were deemed unsatisfactory.

Finally, the temperature range to be considered must be specified. While desulfurization at the gasifier exit temperature is preferable, properly designed heat recovery systems will allow certain temperature adjustments without appreciable efficiency losses. After studying the processes described by Robson et al. (6), we have concluded that desulfurization from 400–1200 °C is of potential interest.

In this study, a single coal composition and gasifier feed mixture are reported. The elemental analysis of each is found in Table I. The fuel is typical of much of the U.S. high-sulfur coal. Gasifier feed analysis corresponds to 59% of the oxygen required for total combustion and a 0.36 molar ratio of steam to air, conditions which are representative of the "third generation" processes described by Robson et al. (6). Only elemental analyses are tabulated as this information alone is necessary for free energy minimization. Chemical composition of the gasifier effluent may be read from Figure 2 of Reference 7.

Characteristics of other fuels and gasification mixtures reported by Stinnett et al. (7) were also examined (8). Differences were found to be minor so that the results reported are applicable to a broad range of low-Btu gas compositions.

### Thermodynamic Analysis

Oxides of the 28 elements listed in Table II were subjected to detailed thermodynamic analysis. These elements were

Table I. Elemental Analysis of Fossil Fuel and Gasifier Feed Mixture

Element	Fuel analysis, mass %	Gasifier feed analysis <sup>a</sup> , atomic %
Hydrogen	5.3	30.1
Carbon	68.5	15.8
Oxygen	8.5	18.6
Nitrogen	1.4	35.1
Sulfur	4.1	0.4
Ash	12.2	—

<sup>a</sup> Ash-free basis.

Table II. Elements Whose Oxides Were Considered in Detailed Thermodynamic Analysis

1. Lithium	11. Iron	20. Cadmium
2. Sodium	12. Cobalt	21. Tin
3. Magnesium	13. Nickel	22. Antimony
4. Aluminum	14. Copper	23. Barium
5. Potassium	15. Zinc	24. Tungsten
6. Calcium	16. Strontium	25. Lead
7. Titanium	17. Zirconium	26. Bismuth
8. Vanadium	18. Molybdenum	27. Lanthanum
9. Chromium	19. Silver	28. Cerium
10. Manganese		

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**Table III. Manganese Compounds Considered in System Mn-C-H-N-O-S**

1. Mn(s)	7. Mn <sub>2</sub> O <sub>3</sub> (s)	13. MnSO <sub>4</sub> (s)
2. Mn(l)	8. α-Mn <sub>3</sub> O <sub>4</sub> (s)	14. Mn <sub>4</sub> N(s) <sup>a</sup>
3. Mn(g)	9. β-Mn <sub>3</sub> O <sub>4</sub> (s)	15. MnCO <sub>3</sub> (s)
4. MnO(s)	10. MnS(s)	16. α-Mn <sub>3</sub> C(s)
5. MnO(g) <sup>a</sup>	11. MnS(l)	17. β-Mn <sub>3</sub> C(s)
6. MnO <sub>2</sub> (s)	12. MnS <sub>2</sub> (s) <sup>a</sup>	

<sup>a</sup> Estimated thermodynamic data were employed for these compounds.

selected after a preliminary screening of the periodic table eliminated nonmetals, radioactive and extremely toxic elements, prohibitively expensive elements, and elements for which sufficient thermodynamic data were unavailable.

The general principles of free energy minimization are discussed by van Zeggeren and Story (9), while the computational procedure used in this study is described by Westmoreland (8). All gases are assumed ideal while condensed species are assumed to form pure phases.

The analysis requires free energy-temperature data for all possible equilibrium species. Possible gaseous species were previously defined by Stinnett et al. (7). In this study, extension of the free energy data base to include solid, liquid, and vapor species associated with the desulfurizing metals was necessary. Altogether, the free energy-temperature functions of 434 species were utilized. As an example, the possible equilibrium compounds considered in the manganese system are listed in Table III. Similar data sets were prepared for the other 27 elements.

Thermodynamic results should always be qualified to reflect the availability and reliability of thermodynamic data. Data for the 434 compounds were compiled from a number of sources (10-14). In certain cases, a portion of the data was estimated; manganese compounds which utilized estimated data are indicated in Table III.

An additional qualification regarding the accuracy of the equilibrium treatment, particularly at low temperature, is in order. Meeting the established thermodynamic criteria should be considered a necessary but not sufficient condition for establishing desulfurization feasibility. Kinetic experiments should follow the thermodynamic screening.

#### Thermodynamic Results

Desulfurization potential was analyzed by minimizing the free energy of a C-H-N-O-S elemental system defined by Table I in the presence of an excess of the metal oxide being evaluated. In this manner, fractional sulfur removal could be determined simultaneously with the stable state of the excess metal. Pressure was fixed at 20 atm while temperature was varied between 360 and 1560 °C.

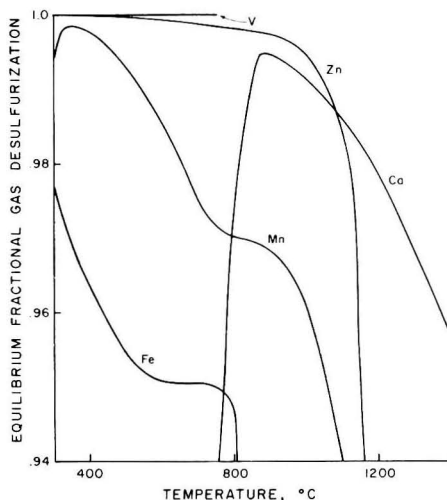
Of the 17 of 28 elements judged unsatisfactory, 13 were rejected because of inadequate desulfurization. Of these, six—Al, Ce, Cr, Mg, Ti, and Zr—formed stable, unreactive oxides (or carbonates) throughout the temperature range. Similarly, the alkali metals were rejected because the stable solids—Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>—were unreactive. It should be noted that initial sulfiding of the alkali metals was predicted near the melting temperature of the carbonate. These cases were rejected under the solid stability criterion. Four additional elements—Ag, La, Ni, and Sb—were rejected because of inadequate desulfurization, although sulfiding may occur below the minimum temperature of interest. Finally, four elements—Bi, Cd, Pb, and Sn—were rejected because excess metal oxide could be reduced to a low-melting metal.

The remaining 11 candidates satisfied thermodynamic criteria over at least a portion of the temperature range.

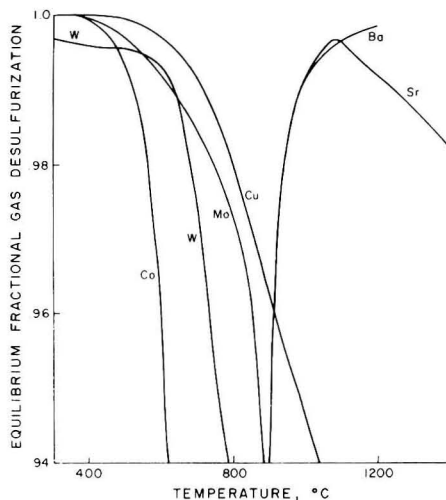
Fractional desulfurization results are summarized in Figures 1 and 2. From Figure 1, it is obvious that manganese, for example, satisfies the 95% desulfurization criterion at all temperatures below 1060 °C. On the other hand, calcium satisfies this requirement only at temperatures above 770 °C. Figure 3 summarizes solid stability results. As an example, consider barium. At low temperature, BaCO<sub>3</sub> is the stable solid form. Sulfiding of the carbonate begins at approximately 800 °C, and from that point to the 1200 °C melting temperature of BaS, simultaneous existence of solids BaS and BaCO<sub>3</sub> is predicted.

By properly combining information from Figures 1-3, the desulfurization potential of each candidate can be established. These results are summarized in the following paragraphs.

Barium: Sulfiding of BaCO<sub>3</sub> begins near 800 °C and reaches the required 95% sulfur removal near 900 °C. From 900 to 1200 °C, the melting point of BaS, all thermodynamic criteria are satisfied. This temperature range is higher than needed using current gasification technology. The behavior of barium and



**Figure 1.** Desulfurization potential of candidate solids



**Figure 2.** Desulfurization potential of candidate solids

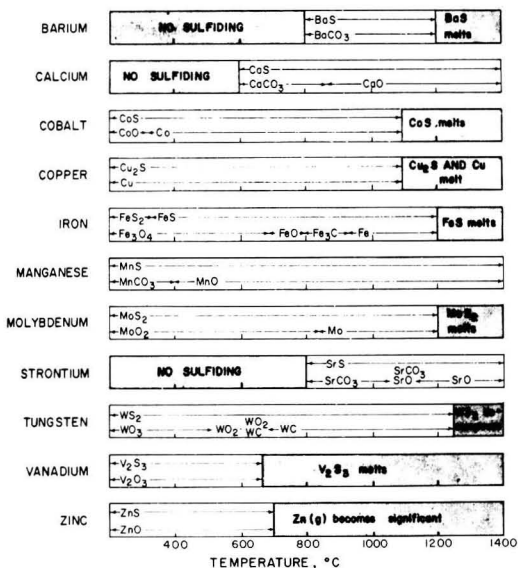


Figure 3. Stable solid phases

calcium are similar but calcium provides a wider applicable temperature range and is less expensive.

**Calcium:** Sulfiding of CaCO<sub>3</sub> begins near 600 °C and reaches the required 95% desulfurization just below 800 °C. Maximum desulfurization capacity occurs near 880 °C, the temperature at which CaCO<sub>3</sub> decomposes to CaO. Note that the CONSOL process (5) being developed reacts half-calcined dolomite, CaCO<sub>3</sub>·MgO, at 900 °C and 15 atm to form CaS·MgO. Perhaps the major drawback to calcium is that use is restricted to temperatures above 800 °C. Lower temperature desulfurization is suitable for many applications without loss of efficiency. Further, materials of construction problems would be reduced at lower temperatures.

**Cobalt:** Cobalt satisfies desulfurization criterion to a maximum temperature of 600 °C with CoS the sulfided product. In the reducing atmosphere of coal gas, excess cobalt would be present as the metal at temperatures in excess of 300 °C.

**Copper:** The behavior of copper and cobalt is similar, although copper maintains 95% desulfurization capability to a temperature in excess of 900 °C. In the reducing atmosphere, excess copper would be present in metallic form over the entire temperature range.

**Iron:** Iron is a suitable desulfurizing material at temperatures up to 700 °C. At these temperatures, Fe<sub>3</sub>O<sub>4</sub> is the stable form of excess iron. The rapid decrease in fractional desulfurization near 700 °C corresponds to Fe<sub>3</sub>O<sub>4</sub> reduction to FeO.

**Manganese:** Oxide stability and high fractional desulfurization are predicted to temperatures in excess of 1000 °C. Below 400 °C, MnCO<sub>3</sub> is the stable solid, while above 400 °C, MnO is stable. Importantly, manganese shows desulfurization

potential in the temperature range of 600–700 °C where metal oxides currently known to be reactive with H<sub>2</sub>S are unsatisfactory.

**Molybdenum:** Molybdenum exhibits satisfactory desulfurization to a temperature in excess of 800 °C. The temperature at which fractional desulfurization drops below 95% corresponds closely to the temperature at which MoO<sub>2</sub> is reduced to the metal.

**Strontium:** The behavior of strontium, barium, and calcium is similar. At low temperature, SrCO<sub>3</sub> is stable and sulfiding does not begin until 800 °C. By 900 °C desulfurization has reached the 95% level and maximum desulfurization occurs near 1100 °C, where SrCO<sub>3</sub> decomposes into the oxide. Calcium would be preferred to strontium because of the wider range of operating temperature.

**Tungsten:** The behavior is similar to molybdenum with desulfurization dropping below 95% near 1000 °C. Excess tungsten may exist in several oxidation states. WO<sub>3</sub> is stable to 550 °C where reduction to WO<sub>2</sub> occurs. Near 600 °C the WO<sub>2</sub> is converted to WC.

**Vanadium:** In the reducing atmosphere, V<sub>2</sub>O<sub>3</sub> is the stable form of the excess metal. Essentially 100% desulfurization, with V<sub>2</sub>S<sub>3</sub> as the sulfided product, is predicted up to the melting temperature of V<sub>2</sub>S<sub>3</sub> near 650 °C.

**Zinc:** On the basis of fractional desulfurization, zinc is acceptable to 1150 °C with ZnS as the sulfided form and ZnO as the stable form of excess zinc. However, zinc is limited to a maximum temperature of approximately 700 °C because of the formation of zinc vapor. Experimental observations in this laboratory have confirmed the formation of zinc vapor in similar atmospheres at temperatures in excess of 700 °C.

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# Cadmium Accrual in Combined Wastewater Treatment–Aquaculture System

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■ Trace amounts of cadmium were added to isolated links of a sewage/seawater–plankton–shellfish food chain employed in a prototype tertiary treatment–aquaculture system in operation at Woods Hole Oceanographic Institution. Accumulation of metal was studied in two types of phytoplankton, a green platyomonad (*Prasinocladus tricorutum*) and a mixture of diatoms (predominantly *Phaeodactylum tricorutum* and *Chaetoceros simplex*), and two species of shellfish, the American oyster (*Crassostrea virginica*) and the hard clam (*Mercenaria mercenaria*). The algae showed a rapid increase in metal concentration until an equilibrium was reached, proportional to the initial concentration introduced. Shellfish species exhibited a continual increase in concentration when exposed to seawater and algae mixtures contaminated with cadmium. Separation of the two pathways of transfer identified the algae as the principal source of accumulation in the aquaculture system. Safe levels of cadmium were evaluated by determining final concentrations of cadmium expected in the shellfish tissue for various algae–shellfish–human food chains.

The combination of aquaculture and tertiary sewage treatment has been suggested as an efficient and potentially profitable means of removing excessive nutrients from municipal secondary effluent. Phosphorus and nitrogen are assimilated by the growth of unicellular algae which, in turn, are fed to shellfish (1). A town of 50,000 people with a 126-acre aquaculture–sewage treatment system could raise an annual crop of over 900 tons of oyster meat or nearly 250,000 bushels of whole oysters, with an estimated worth in today's market upward of \$5 million as a luxury table oyster or \$1 million as canned or frozen meat products (2).

There are three major sources of potential contamination of the shellfish: pathogens, such as amoebic cysts, bacteria, and viruses; organic substances, such as pesticides, phenols, and polychlorinated biphenols, which may be toxic to the culture system, contaminate the products, or make the products unpalatable; or trace metals, which even at subacute levels may lead to long-term, chronic disorders and thus may render the aquaculture crop unfit for human consumption. In this paper we report our analysis of one aspect of the trace metal problem—the ability of a toxic metal, cadmium, to accumulate in the artificial food chain of a tertiary treatment–aquaculture system. Based on the observed rate of uptake, guidelines for safe cadmium concentrations are suggested for the effluent and seawater employed in the system.

Cadmium occurs naturally in flowing seawater, usually cited at less than 0.1 µg/l. (ppb) for unpolluted coastal regions (3). Elevated levels may follow industrial discharge into bays or contamination by municipal wastewater (4). In the tissue of oysters and other shellfish taken from polluted water, higher concentrations of cadmium are found than those from unpolluted water (5, 6). With a cadmium level in seawater as low as 0.05 µg/ml (ppm), Pringle et al. (7) found soft shell clams accumulated cadmium at a rate of 0.1 µg/g wet weight/day.

Little information exists, however, on the rate of accumulation of heavy metals by shellfish under intensive cultivation using municipal wastes as a nutrient source.

## Wastewater Treatment–Aquaculture System

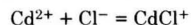
To develop guidelines for safe operation of an aquaculture system, trace amounts of cadmium were added to isolated links of a sewage/seawater–plankton–shellfish food chain employed in a prototype tertiary treatment–aquaculture system in operation at Woods Hole Oceanographic Institution (Figure 1). Secondly treated wastewater, diluted with seawater, makes an excellent medium for growing marine phytoplankton. The phytoplankton is, in turn, removed from the water by filter feeding shellfish, converting the organically fixed nutrients into valuable protein. Nutrients regenerated from faecal deposits of the shellfish are removed by the growth of macroscopic algae in tanks before discharge of the effluent to coastal water.

The effluent is added to filtered seawater at a ratio of 1:4. Phytoplankton cultured in this mixture together with diluting seawater is then introduced into tanks of shellfish at a concentration of 1 part culture to 19 parts 100 µ-filtered seawater.

At this dilution, the particulate carbon content of the seawater, an indicator of the food value to the shellfish, is raised from a normal level of 100 µg carbon/l. to roughly 600 µg carbon/l. More than 80% of the phytoplankton fed to the shellfish originates from nutrients provided by the effluent, and about 1% of the water reaching the shellfish is derived from the secondary effluent. Long-term monitoring by Kerfoot and Jacobs (8) has shown no measurable increase in the cadmium content of tissue of shellfish cultivated in the system. This appears to be due to the low cadmium content of the natural seawater (0.08–0.05 µg/l.) and of the domestic sewage (from 2.3 to 0.5 µg/l. (ppb) used as culture media.

## Pathways of Contamination

Cadmium compounds are quite soluble in excess aqueous halide solutions like seawater (9). The association of chloride ion with cadmium yields the ion pair  $CdCl^+$



Polarographic studies by Baric and Branica (10) of cadmium species in seawater following enrichment have shown that the

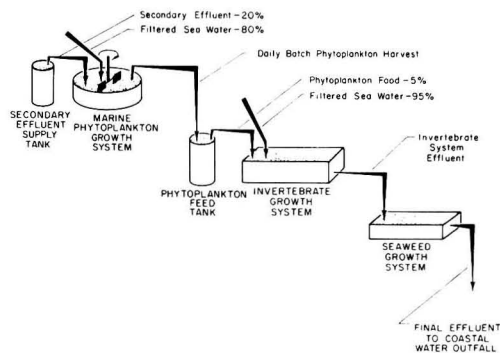


Figure 1. Schematic flow diagram of combined sewage treatment marine aquaculture system [from Goldman et al. (1)]

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metal is predominantly in the form of the monochloro complex. Based on the solubility product of the insoluble hydroxide, Goldberg (17) calculates that 105 mg/l. (ppm) of cadmium can be maintained in solution by the natural chloride content of seawater.

In the artificial environment of the aquaculture system, two sources may provide heavy metals that lead to contamination of shellfish (Figure 2). Metals may be introduced either with the effluent, or in the seawater used for dilution. It is possible that algae and shellfish may then accumulate metallic ions directly from solution by absorption (here indistinguishable from adsorption), or the shellfish may obtain the metal indirectly through ingestion of phytoplankton and detritus containing cadmium. The levels of metal contamination may be modified by varying the dilution of effluent during culture, the harvest time of the algae culture, or the dilution of phytoplankton fed to the shellfish.

In this study, two species of algae and two species of shellfish, under cultivation in the treatment-aquaculture system, were exposed to cadmium. One algae culture was dominated by a green platyomonad, *Prasinocladus subsalsus*, the other by a mixture of diatoms, predominantly *Phaeodactylum tricornutum* and *Chaetoceros simplex*. Culture of the diatoms is preferred during the normal operation of the aquaculture system since they encourage faster growth of the shellfish (Kenneth Tenore—personal communication). The green algae, which are considered undesirable, commonly coat the sides of culture pools and replace the diatoms unless the tanks are cleaned assiduously. The American oyster (*Crassostrea virginica*) and the hard clam (*Merccenaria mercenaria*) were the shellfish species employed in this study. The oysters were obtained from Long Island Oyster Farms, Inc., and the clams removed from beds seaward of Chatham, Mass.

#### Methods and Materials

Phytoplankton was cultured by batch exposure in media specially prepared from Guillard and Ryther's "f" to correspond to secondary effluent (12). A starter monoculture of 100 ml of algae from the treatment tanks was added to the media, and the mixture brought to a final volume of 2 l. In enrichment experiments, a 1000-ppm standard of  $Cd^{2+}$  in double-distilled water was prepared from cadmium iodide salt ( $CdI_2$ ) before dilution with seawater. Then 5 ml of cadmium stock solution, diluted to yield the appropriate concentration, was added to the solution. Batch cultures, prepared in this manner, were placed under fluorescent lights and agitated continuously by magnetic stirring bars at 20 °C. Subsamples or entire cultures were harvested after set intervals of time and centrifuged. The recovered phytoplankton was collected on acid-rinsed membrane filters (3- $\mu$  Nuclepore), rinsed with distilled water, dried, weighed, wet-ashed, and analyzed for total content of cadmium.

For direct exposure of shellfish, the stock cadmium solution was diluted by seawater up to 10 l. The resulting cadmium solution was then mixed at a rate of 7–300 ml/min of seawater

before flowing into 40 × 60-cm fiberglass trays containing oysters and quahogs. The calculated residence time in the tray was 22 min. A control tray received only seawater and phytoplankton as food. At each sampling period, three shellfish were removed, allowed to void their intestinal tracts by placing the animals in clean seawater for 1 h, and then frozen.

To determine the transfer through ingestion, phytoplankton exposed to Cd was resuspended in uncontaminated seawater, fed to shellfish, and then the shellfish were analyzed for accumulation. Algae were cultured in 10-l. carboys enriched with cadmium as previously described. Samples were taken to measure carbon, nitrogen, and hydrogen composition. After 5-day exposure, sufficient to establish equilibria, the algae were removed from solution by continuous centrifuging and then resuspended in 100 ml of uncontaminated seawater. Microscopic examination of a 1-ml aliquot was made following centrifugation to assure that cells were not damaged during removal and resuspension. A second sample of 10 ml was removed for analysis of total cadmium and concentration on a dry weight basis.

Shellfish were fed the contaminated algae by two methods: the resuspended algae were diluted to 10 l., placed in a 12-l. carboy, and added continuously during 24 h to a tray containing shellfish; or apportioned to 500 ml of seawater in 1-l. beakers holding individual shellfish. Periodic sampling of the water was performed to monitor changes in the dissolved cadmium concentration. After a set time or, in the case of individual feeding, when the suspended algae were removed from solution, the shellfish were placed in uncontaminated flowing seawater to allow time to completely void their tracts of ingested matter. The specimens were then frozen prior to digestion and analysis.

For wet ashing, the entire body of an oyster or clam was removed from the shell, rinsed with distilled water, weighed, and transferred to aqua-regia washed 125-ml Erlenmeyer flasks. Phytoplankton was rinsed with distilled water, dried in a warming oven at 50 °C for 24 h, weighed, and added to similar acid-rinsed flasks.

Digestion was performed by adding 10 ml of concentrated nitric acid to the sample. The sample was allowed to stand in acid for 12 h, heated gently to dryness, and allowed to cool. Then 10 ml of 30% hydrogen peroxide was added, and the sample again heated to dryness. After cooling, the sample was redissolved in a 5% nitric acid solution, made up of a standard volume for analysis, and aspirated directly into the atomic absorption spectrophotometer. All analyses were done on a Jarrell-Ash Model 800 atomic absorption spectrophotometer, a double-beam dual-channel instrument with recorder printout (13). Algae were ashed and analyzed following the same procedure as shellfish.

Efficiency of the digestion procedure for shellfish was evaluated by determining recovery and reproducibility. Although some salt error has been noted during analysis of very low concentrations of cadmium in tissue (14), no interference of this nature was encountered during the analysis of algae or shellfish tissue. A known amount of cadmium (10  $\mu$ g) was added to twenty 10-g portions of homogenized oyster tissue, with five untreated samples serving as controls. Recovery of added cadmium averaged  $98.6 \pm 5.6\%$ .

#### Results

**Phytoplankton Uptake of Cadmium.** Unicellular algae constitute the first step in the artificial food chain of the tertiary treatment-aquaculture system. Soluble cadmium introduced into culture tanks with the effluent or present in the dilution seawater may be absorbed at this stage. Figure 3 illustrates uptake observed in a 0.05- $\mu$ g/ml (ppm) solution of cadmium simulating the algal culture tanks. Cadmium was incorporated rather rapidly during the first few hours of ex-

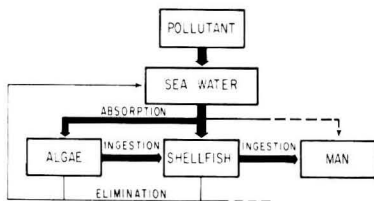


Figure 2. Pathways of accumulation of cadmium in simple algae-shellfish-man food chain of combined wastewater treatment-aquaculture system

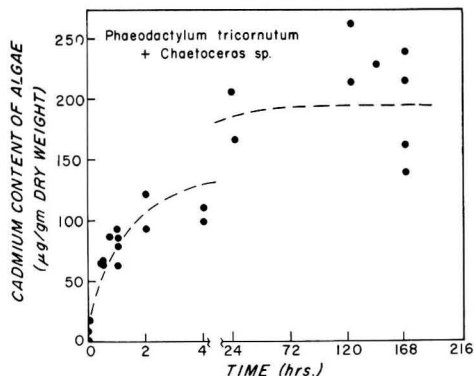


Figure 3. Uptake of cadmium by phytoplankton during culturing

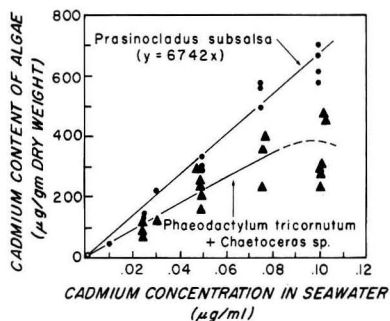


Figure 4. Content of cadmium in tissue of algae removed after average of 5 days of culture

posure and then at a progressively diminishing rate. After 24 h a roughly constant level of cadmium concentration was reached in the cultures. With an average residence time of 2 days for a culture before harvesting, sufficient time has elapsed for a stable level to be established in the algal cells prior to harvesting.

Samples of batches removed 5 days following addition of cadmium showed a proportional increase in the content of cells with increase in concentration in seawater (Figure 4). The green platymonad, *Prasinocladus subsalsa*, showed a greater tendency to accumulate cadmium than the mixed diatom culture of *Phaeodactylum* and *Chaetoceros*. On a dry weight basis, *Prasinocladus* accumulated cadmium to about 6700 times the concentration initially in solution. On the other hand, in the enriched diatom culture, the dry weight of the phytoplankton averaged about 4000 times the initial cadmium concentration in solution.

The total cadmium contained by the algae was calculated for a density of 12,000 µg carbon/l., the normal abundance prior to harvesting. At the carbon content of harvesting, roughly 31% of the total cadmium was bound to particulate material in the *Prasinocladus* culture and 13% to algal cells in the mixed diatom culture. This calculation is based on the measured carbon content of the *Prasinocladus* culture (26.3% of dry weight), somewhat lower than other *Chlorophyceae* (15, 16), and on the *Phaeodactylum* culture (36.5% of dry weight), similar to that reported for the species by Parsons et al. (15). Exposed to a concentration of cadmium of 100 µg/l., about 69 µg of cadmium would persist in solution and 31 µg would be associated with the algae in the green algal culture; whereas 87 µg cadmium in solution and 13 µg cadmium with the algae would occur in the mixed diatom culture.

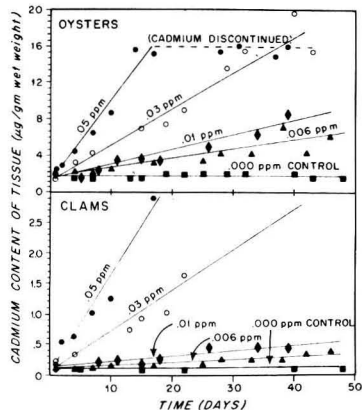


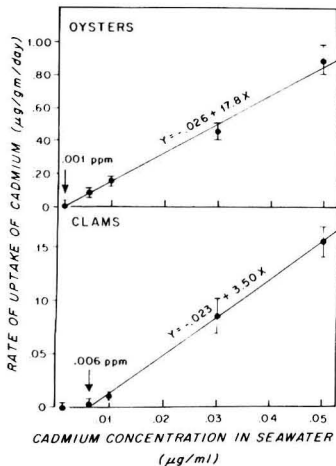
Figure 5. Cadmium content of meat of shellfish removed at different times during continual exposure to contaminated seawater. Each point: mean value of three individuals. Dotted line: when cadmium exposure stopped and oysters flushed with normal seawater

No evidence existed of a threshold concentration at which cadmium assimilation ceased in the *Prasinocladus* culture. Uptake remained a constant proportion of concentration in solution. At the highest concentration studied, 0.10 µg/ml (ppm) cadmium, a slight lessening of uptake was noted in the diatom culture, along with the first indication of toxic effects on growth. However, this avenue of investigation was not pursued further.

The chemical nature of the binding of cadmium to the algal cell is not known, but the cadmium associated with the algal cells is not immediately released into solution upon resuspension of the cultured cells in uncontaminated seawater. Successive sampling of water containing undamaged cells exposed to 0.10 ppm cadmium and with a dry weight concentration of 600 ppm cadmium showed that after 2 h only 10% of the cadmium originally bound to the algal cells was released and would pass through a 3.0-µ filter.

**Shellfish Uptake of Cadmium from Seawater.** Both oysters and clams responded to cadmium enrichment of seawater with a linear accumulation of metal in their tissues for the entire duration of an experiment and over all concentration ranges studied (Figure 5). Originally, the oysters (*Crassostrea virginica*) and clams (*Mercenaria mercenaria*) contained background concentrations of  $1.77 \pm 0.29$  and  $0.09 \pm 0.02$  µg/g (ppm) wet weight of tissue, respectively. Each point in Figure 5 represents the mean of three individual shellfish analyses. The rate of accumulation varied with concentration, the higher the level of cadmium in the seawater the greater the rate of uptake. The addition of 0.03 µg/ml (ppm) cadmium was continued for 67 days without any apparent departure from linearity. No mortality of shellfish that could be related to metal poisoning was recorded with experimental animals at any concentration being studied. After 17-day continuous exposure to seawater containing cadmium, no further metal was added to the 0.05 ppm system. The shellfish were allowed to stand in running seawater for 25 days. Analyses of the oysters during this time showed no measurable decrease in cadmium content of the tissue (Figure 5). Additional studies of oysters and clams showed no detectable elimination of cadmium from animal tissue. These results agree with previously reported long half-lives for cadmium (200 days or longer) in rats, dogs, goats, and man (17-20).

In the shellfish experiments, the concentrations of cadmium added in the seawater were decreased in a stepwise fashion to levels below which no accumulation was detectable. As



**Figure 6.** Rate of uptake of cadmium by shellfish as function of concentration in water

Each central point: slope of linear regression line fitted to points in Figure 4. Width of line:  $\pm$  one standard error. Point at which no rate of increase was measurable marked by arrow

shown in Figure 6, no noticeable uptake of cadmium in the tissue of oysters or clams occurred with concentrations below 0.001 and 0.006  $\mu\text{g}/\text{ml}$  (ppm), respectively. Data points in Figure 6 are the mean rates of uptake calculated by computer fitting of a regression line to each accumulation series in Figure 5.

**Shellfish Uptake via Ingestion of Diatoms.** Early in the investigations of phytoplankton uptake, algae exposed to cadmium could be resuspended in uncontaminated seawater and would retain their original cadmium content for a considerable time. Subsequently, algae were cultured in 10-l. carboys enriched with cadmium as previously described. After 5-day exposure, the algae were removed from solution by continuous centrifuging and then resuspended in 100 ml of uncontaminated seawater. A second sample of 10 ml was removed for analysis of cadmium concentration per dry weight of tissue and total content per ml of algae. Shellfish were then fed the contaminated algae by two techniques: the resuspended algae were placed in a 10-l. carboy with seawater and added daily to a tray containing shellfish; or apportioned 10 or 20 ml resuspended algae to 500 ml seawater in 1-l. beakers holding individual oysters. After a set time or, in the case of individual feeding, when the suspended algae were cleared

from solution, the shellfish were placed in uncontaminated flowing seawater for three days prior to analysis to allow time to completely void their tracts of ingested matter. Experiments on individuals were far easier to interpret since it could be easily seen if feeding occurred, whereas with continual feeding of large groups, the filtering periods of individuals could not be determined.

In general, the shellfish assimilated little of the cadmium presented to them in the algal diet (Table I). The percentage of cadmium persisting following feeding was calculated only when a significant difference was detected between controls and experiments. *Crassostrea* retained from 4.7 to 14.3% of the total cadmium fed in the food, with hardly a noticeable difference between species of algae. Similarly, *Mercenaria* removed 7.0 and 9.1% of the cadmium presented it in the separate diets of the green algal and diatom species, respectively. When both shellfish were fed continuously on *Prasinocladus*, the clams removed 49% that of the oysters. However, the overall mean uptake of the oysters (10%) showed little difference from that of the clams (8.2%), in contrast to the distinctly greater absorption of soluble cadmium in seawater noted earlier for oysters.

### Discussion

**Pathways of Accumulation.** The artificial food chain of a wastewater treatment-aquaculture system concentrates cadmium differently from that which would occur in nature. Figure 7 contrasts the uptake expected by shellfish exposed to cadmium industrially discharged into a coastal bay and cadmium added to the effluent used in the treatment culture system. If the natural seawater is enriched with cadmium, the greatest load of metal is obtained directly through absorption. On the other hand, in the treatment-aquaculture system with effluent as the source of cadmium, the principal means of accumulation is through the ingested algae. Progressive dilution of the effluent by seawater leads to the lessened role of direct absorption as a pathway of contamination of the shellfish. Soluble cadmium introduced into the algae tanks with the effluent is progressively diluted with seawater so that the final concentration in the shellfish tanks is less than  $1/100$  of its original concentration.

To demonstrate the difference, in Figure 7, the expected rate of increase in cadmium content of tissue is compared for 3-g oysters and 5-g clams under natural coastal seawater conditions and in the treatment-aquaculture system. For instance, a 3-g oyster commonly ingests 1.4 mg of carbon per day derived from coastal seawater (21). When feeding on *Prasinocladus*, which has a measured carbon content of 26.3% dry weight, the intake amounts to 0.0053 g dry weight of algae

**Table I. Uptake of Cadmium from Ingested Algae**

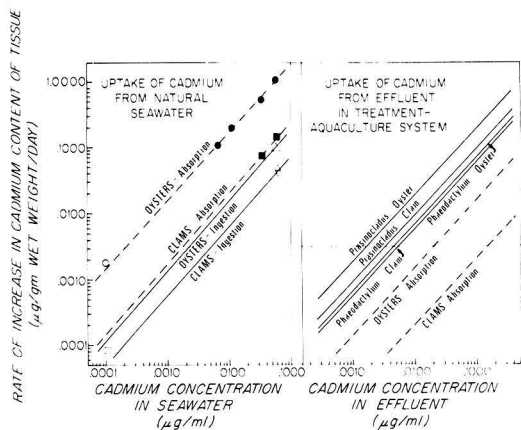
Organism	No. of Individuals	Mean wt, meat	Total $\mu\text{g}$ Cd fed in algae	Final Cd content, ppm wet wt	Significance	% Uptake
<i>Prasinocladus</i> —batch exposure						
Oyster	4	3.29	1.1	1.91 $\pm$ 0.25		
	5	3.41	67.5	2.63 $\pm$ 0.42	$p < 0.025$	7.3
<i>Prasinocladus</i> —continuous exposure						
Oyster	4	4.37	0	1.77 $\pm$ 0.25		
	16	3.82	41.6	3.25 $\pm$ 0.43	$p < 0.02$	14.3
Clam	7	5.95	0	0.08 $\pm$ 0.014		
	4	6.59	41.6	0.48 $\pm$ 0.18	$p < 0.01$	7.0
<i>Phaeodactylum</i> — <i>Chaetoceros</i> —batch exposure						
Oyster	10	7.52	0	1.23 $\pm$ 0.20		
	5	5.38	92.5	3.58 $\pm$ 0.77	$p < 0.01$	13.6
	2	7.86	109.0	2.38 $\pm$ 0.38	$p < 0.01$	4.7
Clam	11	8.63	0	0.21 $\pm$ 0.04		
	4	10.40	10.4	0.15 $\pm$ 0.02	ns	
	2	8.73	92.5	1.18 $\pm$ 0.31	$p < 0.01$	9.1

per day. Exposed to 0.10  $\mu\text{g}/\text{ml}$  (ppm) cadmium in the seawater, the algae would contain 670  $\mu\text{g}$  cadmium/g dry weight. Using the highest retention measured (14.3%), each day a feeding oyster would ingest 3.55  $\mu\text{g}$  of cadmium with only 0.5  $\mu\text{g}$  being retained. Diffused throughout the 3-g weight of the oyster, the projected increase in cadmium content of the tissue would be 0.16  $\mu\text{g}$  cadmium/g day from ingested algae (as indicated by the line marked "OYSTERS—Ingestion" on the left half of Figure 7). Even considering the algae which absorb cadmium the highest and using the greatest measured percent retention, we note ingestion of contaminated algae (by the oysters) under natural seawater conditions contributes only about  $\frac{1}{10}$  of that absorbed directly from solution.

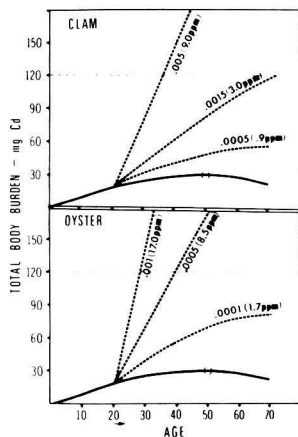
The right half of Figure 7 illustrates the uptake of cadmium with different artificial food chains occurring in the treatment-aquaculture system. Based on specific absorption of the algal species and the mean retention upon ingestion, the daily rate of increase of cadmium is computed for the four possible artificial food chains exposed to different concentrations of cadmium in the effluent used for culture (solid lines). The *Prasinocladus*-oyster food chain exhibits the highest rate of increase of cadmium, whereas the *Phaeodactylum*-clam combination is the poorest amplifier. Because of dilution, the cadmium absorbed directly from solution is less than  $\frac{1}{100}$  the rate expected in natural seawater (dotted lines).

Also, when the lines representing daily uptake of cadmium are extended down to the normal level of cadmium in coastal seawater (0.0001 ppm), they closely approach the rate of increase of cadmium observed in nature. The natural uptake of cadmium in oysters and clams was plotted (open circle and square, Figure 7) by dividing their baseline concentrations, respectively 1.17 and 0.086 ppm, by their approximate age (1000 days). The closeness of the regression line based upon experimental uptake to the estimated natural uptake suggests that the disparity observed in nature between the cadmium content of the oyster and clam may reflect the difference in absorption rates of soluble cadmium.

**Human Uptake and Permissible Guidelines.** To determine permissible levels in the dilution seawater and effluent requires an estimate of the prolonged accumulation of cad-



**Figure 7.** Summary of rate of increase of cadmium in meat of shellfish as function of concentration in seawater and of source of contamination. At left, cadmium introduced in dilution seawater (100  $\mu\text{m}$ -filtered) and to right, in effluent. Dotted lines: accumulation through absorption from solution; solid lines: increase due to ingestion of cadmium associated with algae. Open circle and square to left: natural rate of increase of cadmium in meat of oysters and clams, respectively, found by dividing their background concentrations of cadmium by their approximate age (1000 days) and plotting at average concentration of cadmium found in coastal water (0.0001 ppm). Horizontal dotted lines: rate of increase of cadmium in tissue necessary to yield critical concentration (3.0 ppm) after three years growth



**Figure 8.** Calculated human body burden of cadmium for exposure to cadmium from 40-g daily diet of shellfish

Solid line: observed natural accumulation of cadmium by average U.S. citizen from birth until 70 years of age. Dotted curves: retention from ingestion of different cadmium levels in meat (in parentheses) from age 20, assuming 5% absorption and no elimination. Number preceding cadmium content of meat: concentration in seawater (ppm) necessary to bring about that content after 3 years exposure (1000 days)

mium in the human body from ingestion of shellfish exposed to cadmium contamination. The kidney is considered the critical organ in chronic cadmium poisoning (20). At about 200  $\mu\text{g}/\text{g}$  (ppm) in the renal cortex, tubular proteinuria occurs resulting in renal tubular dysfunction. The load of cadmium in an average human body sufficient to cause this critical level is estimated at 120 mg. The observed accumulation in body burden in different age groups in the United States shows an increase to 30 mg at age 50 and then a decrease to about 21 mg at age 70 (Figure 7) (22). Models depicting the expected cadmium increase in the human body have used a constant daily intake of 50  $\mu\text{g}$  Cd with 5% absorption and an excretion of 0.005% or less to reach 30 mg at age 50.

With the same procedure employed by Kjellstrom et al. (20) in assessing limits of airborne cadmium, the rate of accumulation of cadmium by age was calculated assuming a daily diet of 40 g of shellfish, either ten 4-g oysters or eight 5-g clams. Although the daily intake of shellfish is quite high, it is not too far from an intake expected if shellfish are considered as a staple food. A baseline of the human body burden was based upon the observed natural accumulation of cadmium by a normal U.S. citizen from birth until 70 years of age (20). Assuming a 5% absorption of ingested cadmium with 0% body burden excretion, the yearly amount of cadmium absorbed from a 40 g/day diet of each shellfish was added to the baseline level. As the concentration of cadmium increases in the tissue of the shellfish due to long-term exposure to higher concentrations of cadmium in seawater, the body burden of the human consumer rises rapidly (Figure 8).

To determine recommended levels of cadmium in the municipal effluent and dilution seawater used for aquaculture purposes, the concentration in solution sufficient to yield the critical content in a 3-year-old shellfish was calculated from Figure 7. A 40 g/day diet begun at age 20 with a concentration of 3.0  $\mu\text{g}$  cadmium/g of meat would be enough to elevate the human body burden to 120 mg by age 70. With an average age of 3 years or 1000 days for simplicity, a rate of increase of 0.003  $\mu\text{g}$  cadmium/day would be sufficient to yield the critical concentration in the shellfish. (This critical rate of increase is indicated by the horizontal dotted line on Figure 6.) A background contamination of 0.0002 and 0.0015  $\mu\text{g}/\text{ml}$  (ppm) in the dilution seawater would raise the cadmium content of



**Table II. Concentration of Cadmium (PPM) in Solution Sufficient to Yield Critical Concentration in Shellfish Consumed at 40 G/Day from Age 20 to Age 70**

	Source of contamination		
	Dilution seawater	Effluent	
		<i>Prasinocladus</i>	<i>Phaeodactylum-Chaetoceros</i>
Oysters	0.0002	0.001	0.004
Clams	0.0015	0.003	0.005

the meat of the oysters and clams, respectively, to the critical concentration of 3.0 µg cadmium/g of meat (Table II), whereas a concentration in the municipal effluent of 0.001 or 0.004 µg/ml would presumably reach the same content in oysters depending on whether *Prasinocladus* or the diatom mixture of *Phaeodactylum-Chaetoceros* is cultured to feed the shellfish. With clams the critical concentrations in effluent would be 0.003 and 0.005 ppm, respectively, for culture of *Prasinocladus* and the mixture of diatoms.

A comparison between the critical water concentrations in the effluent and dilution seawater points out the importance of maintaining uncontaminated seawater for dilution. Almost an order of magnitude higher cadmium concentration can be tolerated in the effluent if the dilution seawater is relatively free of cadmium enrichment. Also, if oysters are raised with a diatom mixture, it is important to avoid contamination of the culture by green algae, such as *Prasinocladus*, since the rate of cadmium uptake by the oysters would increase substantially. Although these calculations are, at best, conservative estimates of the upper limits of cadmium which should be maintained for safe shellfish products, they provide a rational basis for decisions of the suitability of effluent sources and dilution seawater to be used in an effluent treatment-marine aquaculture system.

#### Acknowledgment

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# Thermal Decomposition of Manganese Sulfate Pellets

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■ Single pellets of finely ground manganese sulfate were decomposed in nitrogen at 805–905 °C and atmospheric pressure, and reaction rates were measured. The reaction proceeded in topochemical fashion with  $Mn_3O_4$  as the oxide product. Sintering of unreacted pellets occurred during heating, reducing the specific surface area by about 75%. Once reaction began, the specific surface area increased with conversion, reflecting that the porous product layer had a higher specific surface area than the sintered reactant. A topochemical mass transfer model satisfactorily predicted the rate of decomposition and indicated that at 950–1000 °C, the  $SO_2$  concentration in the product gas is sufficient for use in sulfuric acid production.

During recent years, attention has been focused on the development of dry processes for removing  $SO_2$  from flue gases. An attractive possibility is absorption on manganese oxides with subsequent regeneration of the  $MnSO_4$ . Such a process was developed by the U.S. Bureau of Mines (1) in 1961 and successfully tested on pilot and semicommercial scales (2, 3) by the Mitsubishi Co. of Japan. In the Japanese process, chemical regeneration produces by-products which are of little commercial value in the United States. A promising alternate route to regenerate the spent manganese oxide is thermal decomposition. There have been a few studies on the decomposition of manganese sulfate.

Ingraham and Marier (4) measured the rate of decomposition of  $MnSO_4$  in  $N_2$  and  $O_2$  at atmospheric pressure and temperatures from 800–900 °C. The products of decomposition were  $Mn_3O_4$  in  $N_2$  and  $Mn_2O_3$  in  $O_2$ . From initial rates, apparent activation energies of  $51 \pm 2$  and  $62 \pm 2$  kcal/mol were computed for the  $N_2$  and  $O_2$  reactions, respectively. A second group of experiments at 950 °C showed that the initial rate in  $N_2$  is reduced by introducing  $O_2$  or  $SO_2$ , with the  $SO_2$  having the more pronounced effect. Interpretation of data was limited to qualitative conclusions concerning the stoichiometry of the decomposition process at 950 °C and the effect of  $N_2$  flow rate and accumulation of  $Mn_3O_4$  product on the kinetics.

Pechkovskii (5) studied the decomposition of  $MnSO_4$  in  $N_2$ ,  $N_2$  plus 10%  $O_2$ , and air at temperatures from 800–1000 °C. Operating pressure was not reported. He concluded that the presence of  $O_2$  decreases the reaction rate and the solid decomposition product in air was  $Mn_3O_4$  above 950 °C, but below 950 °C a mixture of  $Mn_2O_3$  and  $Mn_3O_4$  was produced. In  $N_2$  and  $N_2$  plus 10%  $O_2$ ,  $Mn_3O_4$  was reported to be the decomposition product.

Thermogravimetric analyses by Ostroff and Sanderson (6) and Cueilleron and Hartmanshenn (7) revealed that the decomposition product in air below 900 °C was  $Mn_3O_4$  in agreement with results obtained by the U.S. Bureau of Mines (8) but contrary to Pechkovskii's findings. Other investigators (9–11) were concerned with the thermodynamics of the  $MnSO_4$  decomposition process.

None of these provided sufficient data to allow formulation of a kinetic model for the system. Therefore, to evaluate the thermal decomposition route, it was necessary to perform a more thorough kinetic investigation. Nitrogen was used as the decomposition gas, and particular attention was focused on

the effects of temperature, porosity, particle size, identification of reaction products, and the possibility of producing sulfuric acid as a by-product. Single spherical pellets of  $MnSO_4$  were employed to obtain the kinetic data. Pelletized  $MnSO_4$  was selected for two reasons. Some form of pelletized material would be used in practice, and virgin  $MnSO_4$  would yield the maximum concentration of  $SO_2$  that could be expected in the product gas stream.

## Selection of Thermal Decomposition Route

Regeneration by thermal decomposition was selected after considering a number of alternatives including electrolysis, regenerating gases, and solid reductants. The direct electrolytic method proposed by Bienstock et al. (1) was dropped from consideration on the basis of the Bureau's results which showed that by-product acid was weak, contaminated with Mn ions, and that the regenerated absorbent had a reduced  $SO_2$  absorption activity. An indirect electrolytic technique also developed by the U.S. Bureau of Mines (1) was not given further consideration because a patent (12) has been granted and the absorbent formed was soft and crumbled easily, making attrition losses a critical factor in the design of industrial gas cleaning equipment.

Use of regenerating gases and carbon was evaluated thermodynamically on the basis of Mah's (13) data. Regenerating gases considered included  $CO$ ,  $H_2$ ,  $HCl$ ,  $HF$ ,  $HBr$ ,  $HI$ , and steam. The results showed that the reaction of  $C$ ,  $H_2$ ,  $CO$ , or mixtures of  $CO$  and  $H_2$  with  $MnSO_4$  is very favorable from the viewpoint of thermodynamics. However, phase diagrams developed for the  $Mn-S-C-O$  system indicated that in addition to  $MnO$  the formation of  $MnS$  is possible. That  $MnS$  is produced has been confirmed by the U.S. Bureau of Mines (8, 14) and others (15, 16). Pechkovskii et al. (15) postulated that  $MnS$  is the end product of a series reaction in which  $MnO$  is an intermediate. On that basis, the sulfide content would increase from regeneration to regeneration.

Experiments were conducted at the U.S. Bureau of Mines (17) to determine the effect of repeated regeneration on absorption capacity and  $MnS$  content. Five different series of experiments were performed using a reducing gas containing 40%  $CO$  and 60% steam at temperatures from 600–750 °C. The number of passes per series varied from 6–10. There was a decline in activity following regeneration in each series. For example, an 84% decrease was observed for the 10-pass series. A limited number of phase and sulfur analyses indicated an increase in sulfide content for some of the series and decrease for others. The overall result, nevertheless, confirmed the reduced activity of the regenerated solid and the continuing presence of the sulfide phase. Consequently, the use of reductants was eliminated from further consideration in the present work.

Two prime factors involved in selection of thermal decomposition were the reported absence of a sulfide phase in previous investigations (4, 5, 9) and the high single-pass activity reported by the U.S. Bureau of Mines (8) during regeneration by thermal decomposition in air at 900 °C. The single-pass activity for air (29.8 g  $SO_2$ /100 g absorbent) compared quite favorably with the highest single-pass activity (34.0 g  $SO_2$ /100 g absorbent) reported for  $CO$  at 600 °C (8).

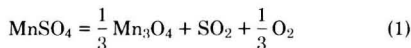
## Theory

Observations of reacted pellets show that under the conditions studied here the decomposition of  $MnSO_4$  occurs to

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pochemically. Therefore, a topochemical model with film and intraparticle diffusion is proposed for the decomposition of spherical particles. The model is structured on the following assumptions:

- The decomposition reaction is represented by the chemical equation



or symbolically by

$$\text{S(solid)} = \text{S'(solid)} + a\text{A(gas)} + b\text{B(gas)} \quad (2)$$

and proceeds in a topochemical manner with respect to the pellet. Although topochemical behavior on the grain level has been demonstrated for the majority of decomposition reactions, there is no a priori reason that the same should necessarily be true on the pellet level.

- The rate of decomposition is controlled by the rate of diffusion of product gas through the oxide product layer and the boundary layer surrounding the pellet.

- The pellet, as demonstrated experimentally, retains its original dimensions.

- The pseudo-steady state approximation is valid.
- The effective diffusivity and mass transfer coefficient are constant.

- The concentration of  $\text{SO}_2$  in the bulk gas stream that is effective for driving mass transfer is defined through an averaging factor  $\alpha$  taken to be the arithmetic average of the inlet gas and a perfectly mixed exit gas. Thus, when the inlet gas is  $\text{SO}_2$ -free, the bulk gas concentration is

$$C_{AO} = \frac{\alpha W_A}{v} = \frac{0.5 W_A}{v} \quad (3)$$

The equation of continuity for component  $A$  in the product layer is

$$D_{eA} \left( \frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} \right) = 0, \quad r_o > r > r_c \quad (4)$$

with the boundary conditions:

$$D_{eA} \left( \frac{dC_A}{dr} \right) = k_{MA} (C_{AO} - C_{AS}) \text{ and } C_A = C_{AS} \text{ at } r = r_o \quad (5)$$

$$D_{eA} \left( \frac{dC_A}{dr} \right) = C_{SO} \frac{dr_c}{dt}, \text{ and } C_A = C_{AC^*} \text{ at } r = r_c \quad (6)$$

The solution of Equation 3 expressed as a relationship between time  $t$  and fractional conversion  $z$  is

$$\frac{t}{A} = [1 + 2(1 - z) - 3(1 - z)^{2/3}] + \frac{Bz}{A} \quad (7)$$

where

$$A = \frac{r_o^2 C_{SO}}{6 D_{eA} C_{AC^*}}$$

$$B = \frac{r_o C_{SO}}{3 k_{MA} C_{AC^*}} \left( 1 + \frac{4 \pi \alpha r_o^2 k_{MA}}{v} \right)$$

The Chapman-Enskog theory (18) and the Ranz-Marshall correlation (19) can be used to estimate the values of the molecular diffusion coefficient and the film mass transfer coefficient. The effective diffusivity through the oxide product layer can be estimated from the relationship (20)

$$\frac{D_{eA}}{D_A} = \frac{\epsilon_D}{\tau} \quad (8)$$

using a value of 2 for the tortuosity factor  $\tau$ .

### Experimental

**Materials.** The manganese sulfate used in the experiments was reagent-grade monohydrated material procured from Fisher Scientific Co. Anhydrous  $\text{MnSO}_4$  was prepared by

heating the monohydrate in a furnace for 24 h at a temperature between 400 and 450 °C. Individual samples of dry powder weighing  $425 \pm 2$  and  $840 \pm 2$  mg were pressed by stainless steel dies into spherical pellets,  $\frac{5}{16}$  in. (0.795 cm) and  $\frac{3}{8}$  in. (0.953 cm) in diameter. Pellets were produced by applying a uniform pressure with a hand-operated press. Dense pellets were made from the hand-pressed pellets by means of an isostatic press. Hand-pressed pellets had porosities of 45.1–47.2% and were classified as porous. The porosities of dense pellets varied from 21.6–29.6%.

Gases used in the experiments included high-purity He,  $\text{N}_2$ ,  $\text{O}_2$ , and anhydrous  $\text{SO}_2$ . Various mixtures of these gases were prepared in a blending unit. Compositions of the blended mixtures were determined by gas chromatography and wet chemistry (iodometric determinations for  $\text{SO}_2$  and Orsat analyses for  $\text{O}_2$ ).

**Apparatus.** The essential features of the apparatus are represented in Figure 1. Control and measurement of gas flows were accomplished by differential flow controllers and rotameters. The rotameters were calibrated to an accuracy of  $\pm 1\%$ . Cylinder helium served as the source of chromatograph carrier gas in addition to being used to protect the weighing mechanism and purge its housing.

Decomposition was carried out in a Vycor combustion tube heated by a vertically mounted furnace. Details of the reactor are shown in Figure 2. The lower section of the tube packed with  $\frac{3}{16}$ -in. (0.476-cm) spheres of sintered alumina and zirconium oxide served as the preheating zone. A  $\frac{1}{8}$ -in. (0.318-cm) stainless steel sheathed Chromel-Alumel thermocouple measured the bulk gas temperature. This temperature was continuously recorded and seldom varied by more than  $\pm \frac{1}{4}$  °C during an experiment. The manganese sulfate sample was placed in a basket constructed from 6-mil (0.152-mm) platinum wire, and the basket was suspended in the reactor by a 2-mil (0.051-mm) platinum wire connected to a Cahn RG electrobalance. The balance was sensitive to an 0.14- $\mu\text{g}$  weight change and had a capacity of 2.5 g. The weight of the sample was continuously recorded on a Leeds and Northrup Speedomax recorder.

Product gas was analyzed with an on-line gas chromatograph using a 6-in. (15.24-cm) long silica gel column for  $\text{SO}_2$  and a 6-ft (1.83-m) long type 5A molecular sieve column for  $\text{O}_2$  and  $\text{N}_2$ .

**Procedure.** The balance was calibrated before each run. Then the pellet was suspended in the reactor, and the reaction tube was sealed. A helium purge through the balance housing and a nitrogen purge through the reaction tube were begun and continued until no traces of oxygen from the system were detected by the chromatograph. On completion of the purge, data for calibrating the chromatograph were taken by passing blended gas mixtures of known composition through the reactor.

At this point, the reactor temperature was raised to 200 °C and maintained there for 1 h to expel any moisture adsorbed by the hydrophilic  $\text{MnSO}_4$  during storage. Occurrence of decomposition during final heating to the reaction temperature was prevented by passing an equilibrated  $\text{SO}_2$ - $\text{SO}_3$ - $\text{O}_2$  mixture through the reactor. Sulfur trioxide was produced by contact between the 5% platinumized asbestos catalyst and the  $\text{SO}_2$ - $\text{O}_2$  heat-up gas. Nitrogen flow was initiated after the furnace temperature stabilized at the control point. Decomposition usually began within 30–60 min after the start of nitrogen flow.

A nitrogen flow rate of 60 std ml/min (21 °C, 1 atm) was used in all experiments with one exception in which a flow rate of 100 std ml/min was employed. A low nitrogen flow rate was used to maximize the  $\text{SO}_2$  concentration in the product gas, thus testing its suitability for the production of sulfuric acid (21).

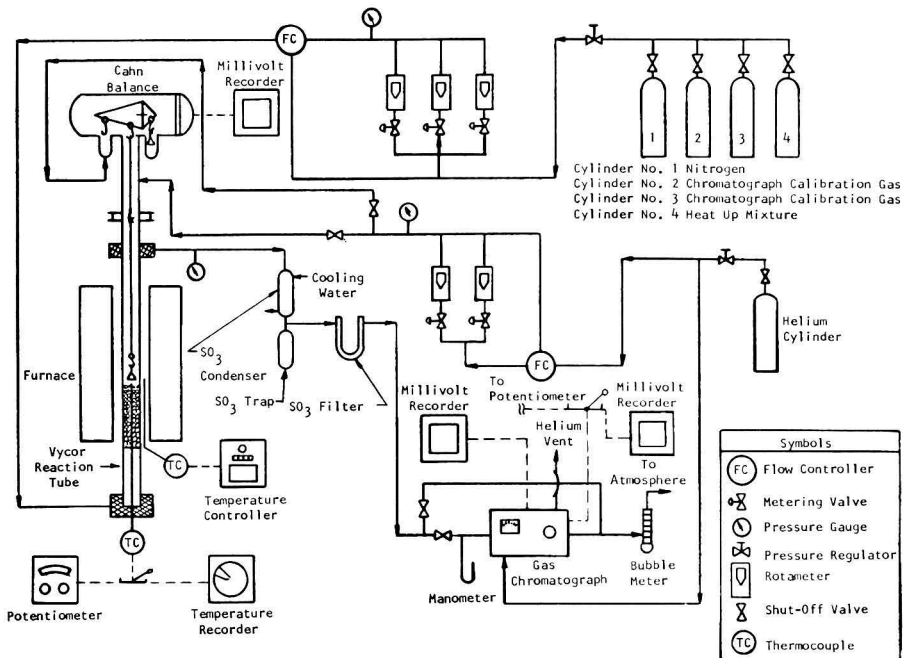


Figure 1. Flow sheet of decomposition equipment

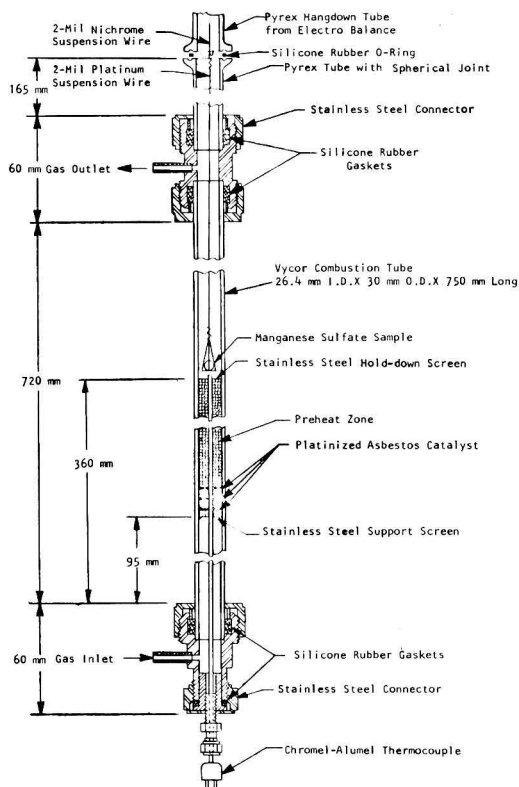


Figure 2. Decomposition reactor

Exploratory runs using both dense and porous pellets were conducted to establish the temperature range for later experiments. The low end of the temperature range ( $\sim 800^\circ\text{C}$ ) was investigated with a heat-up mixture containing 6%  $\text{SO}_2$ , 3%  $\text{O}_2$ , and 91%  $\text{N}_2$ . The data showed that at temperatures below  $800^\circ\text{C}$ , the decomposition proceeded at a rate much too slow for practical purposes. On the high side of the temperature range, runs were made at 925, 950, and  $975^\circ\text{C}$  in the furnace with a 2:1  $\text{SO}_2$ - $\text{O}_2$  heat-up gas. Decomposition occurred in the last two cases during the heat-up period. Consequently, a temperature range from  $805$ – $905^\circ\text{C}$  in the reactor was selected for this study, and a 2:1  $\text{SO}_2$ - $\text{O}_2$  heat-up mixture was used in all subsequent experiments.

In a separate run, the temperature at the center of a dense pellet was measured by a miniature thermocouple, 14 mils (0.355 mm) in diameter, inserted into the pellet. Since the thermocouple's extension wires were used for support, a simultaneous weight measurement could not be made.

### Results and Discussion

**X-ray Diffraction Analyses.** To determine the nature of the solid product, x-ray diffraction patterns were obtained on a number of partially reacted specimens. Prior to x-ray analyses, the pellets were sectioned and examined visually and microscopically. These examinations revealed that a typical pellet was composed of a white inner core surrounded by a reddish-brown layer. Consequently, separate analyses were made of the core and surrounding layer of each pellet. In addition, a composite sample from each pellet was analyzed. Data from 27 analyses showed that:  $\text{Mn}_3\text{O}_4$  was the sole solid product; the inner core was  $\text{MnSO}_4$  contaminated in some cases with trace amounts of oxide; the outer layer was  $\text{Mn}_3\text{O}_4$  contaminated in some cases with traces of sulfate; and the composite samples were consistent with the extent of decomposition—i.e., in cases where the pellet was 30% decomposed,  $\text{MnSO}_4$  was reported to be the major phase and  $\text{Mn}_3\text{O}_4$

the semimajor phase, and the reverse was true at the 80% decomposition level.

**Microscopic Examination.** The distinct product-reactant interface, as seen by the scanning electron microscope at high contrast, is shown in Figure 3. The typical sponge-like, porous appearance of the product layer is shown in Figure 4, and the grainy, sintered appearance of the unreacted  $\text{MnSO}_4$  in Figure 5. These same characteristics were observed in a number of both porous and dense pellets.

A topochemical reaction, by definition, occurs only at the boundary separating the reactant and product. In reality, the interface usually appears as a zone of finite thickness. The maximum thickness of this zone, based on scanning electron microscope photographs, was less than 1% of the pellet radius. The radius of the unreacted core was determined with the aid of an optical microscope. Some deviation from a spherical core was observed, but the extent was not significant. Fractional conversion was computed from the core and pellet radii by means of the relationship

$$z = 1 - \left(\frac{r_c}{r_o}\right)^3 \quad (9)$$

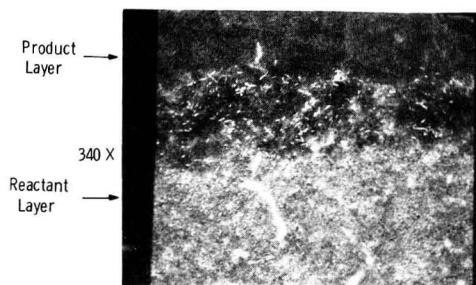


Figure 3. Scanning electron microscope photograph of product-reactant interface (high contrast)

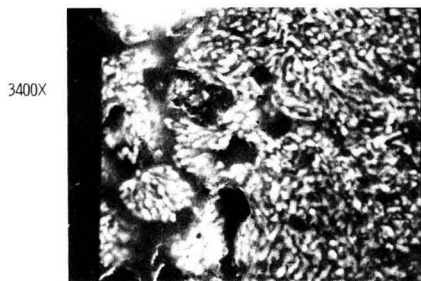


Figure 4. Scanning electron microscope photograph of product layer

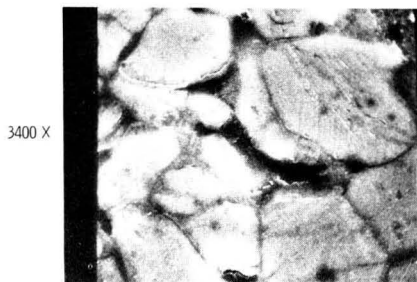


Figure 5. Scanning electron microscope photograph of reactant

The fractional decompositions so calculated were compared with those obtained from data on weight loss. In all cases, the results given by Equation 9 tended to be higher than those obtained from weight loss with a maximum difference of about 5% conversion. That is not unexpected, however, since it is very difficult to cut a pellet exactly across the equator. If the cut is not exact, the observed  $r_c$  is too small, thus increasing the value of  $z$  computed from Equation 9.

**Chromatographic Data.** Chromatographic data were recorded in runs TR-1 through TR-5 (the TR prefix denotes thermal regeneration) at bulk gas temperatures ranging from 807.3 to 815.5 °C. In these runs the reaction was stopped at different levels of conversion. The average molar ratio of  $\text{SO}_2$  to  $\text{O}_2$  in the product gas of runs TR-2 through TR-5 in which a nitrogen flow of 60 std ml/min was used varied from 3.04 to 3.16. For run TR-1 with a nitrogen flow of 100 std ml/min, the ratio was 3.31. These results indicate that Equation 1, which shows an  $\text{SO}_2$  to  $\text{O}_2$  ratio of 3, effectively represents the reaction path and that the presence of  $\text{SO}_3$  may be neglected. Furthermore, according to the equilibrium data of Stern and Weise (22) at 1100 °K, the ratio of  $\text{SO}_3$  to  $\text{SO}_2$  is 0.0992 and that of  $\text{SO}_2$  to  $\text{O}_2$  is 3.15. This indicates that the equilibrium partial pressure of  $\text{SO}_3$ , although not zero, is small in comparison to that of  $\text{SO}_2$ . In subsequent analysis of kinetic data the decomposition reaction was assumed to follow Equation 1, and no chromatographic data were collected for subsequent runs.

**Surface Area Measurements.** Surface area measurements were made of unreacted pellets, pellets heated to temperatures up to 800 °C with little or no decomposition, and partially decomposed pellets. All pellets were prepared for measurement by degassing at 300 °C under high vacuum for a minimum of 4 h.

The specific surface areas of three unreacted porous pellets ( $\epsilon \cong 0.45$ ) varied from 1.40 to 2.17  $\text{m}^2/\text{g}$ , and of three unreacted dense pellets ( $\epsilon \cong 0.25$ ) from 2.86 to 4.72  $\text{m}^2/\text{g}$ . That a dense pellet has greater surface area than a porous pellet appears to indicate that additional pores are created during isostatic compression.

The second set of measurements was made on a group of unreacted porous pellets which had been heated to temperatures from 600–850 °C in the absence of heat-up gas and removed from the furnace within 5 min after the set temperature was reached. The specific surface area was reduced to 0.99  $\text{m}^2/\text{g}$  at 600 °C, 0.84  $\text{m}^2/\text{g}$  at 700 °C, and 0.68  $\text{m}^2/\text{g}$  at 800 °C. The factors most likely responsible for the substantial decrease in surface area are the sintering of grains and closing of pores. As the grains agglomerate, the area exposed to the adsorbate is decreased. Similarly, if pore necks close, certain passages in the particle become unaccessible.

The final set of measurements of reacted porous pellets revealed that the specific surface area increased with conversion. At 830 °C, the specific surface area increased from 0.87  $\text{m}^2/\text{g}$  at 33% conversion to 2.08  $\text{m}^2/\text{g}$  at 91% conversion. At 875 °C the increase was from 0.81  $\text{m}^2/\text{g}$  at 12% conversion to 3.07  $\text{m}^2/\text{g}$  at 92% conversion.

A few measurements of heated and reacted dense pellets showed similar reduction in specific surface area upon heating and the trend toward increasing surface area with conversion. These results indicate that the product layer has a higher specific surface area than the sintered reactant.

**Analysis of Kinetic Data.** A total of 31 kinetic runs was made with porous and dense pellets at atmospheric pressure and temperatures of 805–905 °C. Figures 6 and 7 show typical conversion-time curves for dense and porous pellets.

After the switch from heat-up gas to  $\text{N}_2$ , a long induction period (sometimes in excess of an hour) was observed in which no decomposition occurred. On the other hand, no induction period was observed during experiments conducted in the



absence of heat-up mixture. These experiments were performed for the purpose of obtaining data on surface area. Based on these observations, it was suspected that during the heat-up period the pellet might have become "saturated" by the heat-up gas and that decomposition could not begin until the heat-up gas diffused out of the pellet. To investigate this possibility, an experiment was conducted without a pellet in the reactor to determine the decrease in SO<sub>2</sub> and O<sub>2</sub> concentrations during a nitrogen purge (60 std ml/min) of a 6% SO<sub>2</sub>, 3% O<sub>2</sub>, and a 91% N<sub>2</sub> heat-up gas. Based on these results, an estimate of the amount of SO<sub>2</sub> leaving the pellet by diffusion as a function of time was obtained by utilizing a solution of the diffusion equation (23) for a sphere with a uniform initial concentration and a time-dependent surface concentration. The calculation showed that a period in excess of 1 h was required for complete depletion of the heat-up gas within the pellet. On the other hand, if the surface concentration of SO<sub>2</sub> were zero, only several minutes would be required. This result appears to support the explanation for the observed induction period. It is also consistent with Marier's (24) observation that application of a vacuum significantly reduces the length of the induction period.

As seen in Figures 6 and 7, after the start of decomposition, the rate of conversion increases to an approximately constant value and then decreases gradually with time. This was characteristic of all runs. The initial transient behavior appears to reflect a continuation of the phenomena responsible for the occurrence of the induction period. If the pellet were not initially saturated with heat-up gas, the decomposition would have begun at an initial rate determined solely by the transport resistance in the boundary layer surrounding the

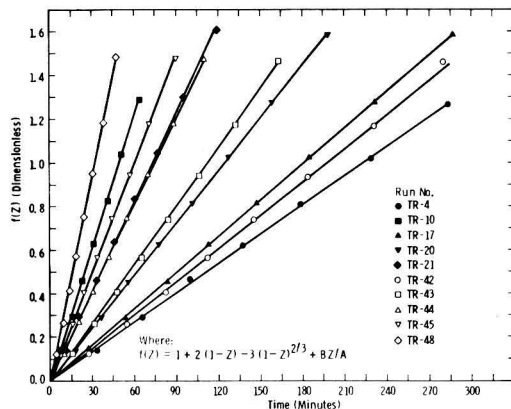


Figure 8. Evaluation of proposed model for dense pellet conversion vs. time data

pellet and continued at a gradually decreasing rate. To correct for the observed transient behavior which occurred up to a maximum of 8% conversion, the experimental curve for conversions greater than 8% was extrapolated. The time at which this extrapolation reached zero conversion was taken to be the starting point of the reaction.

Evaluation of the proposed model was performed in accordance with Equation 7. The value of

$$\frac{B}{A} = \frac{2 D_{cA}}{k_{MA} r_o} \left( 1 + \frac{2 \pi r_o^2 k_{MA}}{V} \right) \quad (10)$$

for each run was calculated using values of  $k_{MA}$  and  $D_{cA}$  from the correlations previously cited. With the known value of  $B/A$  and experimental conversion substituted, the right-hand side of Equation 7 was plotted against the time of reaction, as shown in Figure 8 for dense pellets. The data points for each run do fall on a straight line. This is equally true for porous pellets. Values of the coefficient  $A$  computed from the slopes of the lines are presented in Table I. Also presented are the

Run No.	Average Pellet Diameter (CM)	Sample Weight (MG)	Porosity of Unreacted Pellet	Flow Rate (CC/Min)	Bulk Gas Temperature (°C)
○ TR-42	0.679	414.7	0.219	60.0	812.3
○ TR-43	0.679	416.0	0.216	60.0	838.2
○ TR-44	0.681	418.2	0.222	60.0	863.8
△ TR-45	0.679	415.3	0.217	60.0	880.3
■ TR-48	0.679	412.9	0.222	60.0	905.0

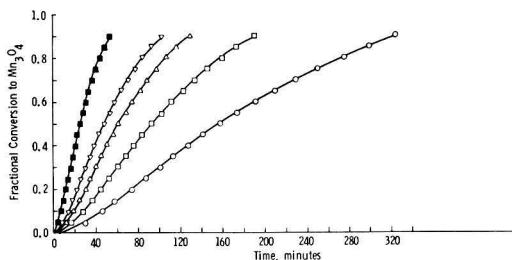


Figure 6. Conversion vs. time data for dense pellets

Run No.	Average Pellet Diameter (CM)	Sample Weight (MG)	Porosity of Unreacted Pellet	Flow Rate (CC/Min)	Bulk Gas Temperature (°C)
○ TR-1	0.936	757.5	0.456	100.0	807.3
○ TR-2	0.962	816.0	0.460	60.0	807.5
△ TR-13	0.962	815.0	0.460	60.0	831.5
▽ TR-15	0.962	808.0	0.465	60.0	854.0
● TR-16	0.962	818.0	0.458	60.0	877.5
■ TR-8	0.962	815.1	0.460	60.0	896.0

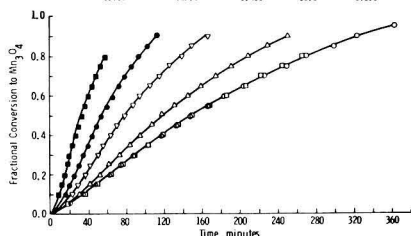
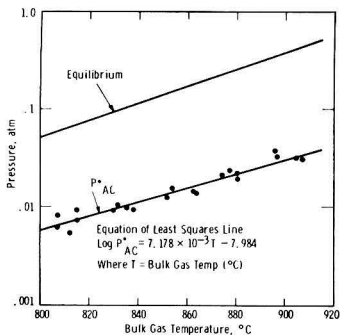


Figure 7. Conversion vs. time data for porous pellets

Table I. Summary of Parameters Obtained from Proposed Model

Run no.	Bulk gas temp, °C	Diffusion resistance coeff, A, min	Apparent decomposition press of SO <sub>2</sub> at reacting interface, P <sub>AC</sub> (atm) × 10 <sup>2</sup>
TR-1	807.3	207.96	0.622
TR-2	807.5	166.67	0.814
TR-4	815.5	224.22	0.740
TR-8	896.0	34.04	3.784
TR-10	897.0	49.73	3.291
TR-13	831.5	126.61	1.055
TR-15	854.0	82.12	1.588
TR-16	877.5	55.19	2.354
TR-17	830.0	181.69	0.933
TR-20	852.0	125.42	1.272
TR-21	874.5	73.04	2.144
TR-27	815.3	112.99	0.933
TR-32	835.5	86.03	0.963
TR-39	862.8	56.81	1.470
TR-40	880.8	42.94	1.914
TR-41	907.8	26.28	3.103
TR-42	812.3	198.33	0.543
TR-43	838.2	112.84	0.944
TR-44	863.8	75.08	1.394
TR-45	880.3	60.55	1.716
TR-48	905.0	32.15	3.166



**Figure 9.** Comparison of equilibrium decomposition pressure of  $\text{SO}_2$  from data of Stern and Weise with apparent decomposition pressure based on proposed model

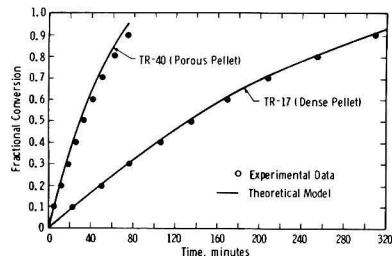
apparent decomposition pressures of  $\text{SO}_2$  at the reacting interface,  $P_{AC}^* = RTC_{AC}^*$ , computed from the coefficient  $A$ . These values are different from the equilibrium pressures (22), and the difference is illustrated in Figure 9. That the ratio of the apparent decomposition pressure to equilibrium pressure is nearly constant and much less than unity may suggest the formation of an intermediate  $\text{Mn}_3\text{O}_4$  structure with an activity less than unity. The intermediate slowly transforms into the stable form for which the thermodynamic data were obtained. This point of view is consistent with the results of an equilibrium study of the decomposition of  $\text{MnSO}_4$  to  $\text{Mn}_3\text{O}_4$ , by Ingraham (9) who reported that at a given temperature approximately 24 h were required before the pressure in the apparatus reached steady state. Another probable explanation is that the apparent decomposition pressure is that at the grain surface, which if the grain is porous, would be lower than equilibrium.

The possibility of temperature effect was investigated by inserting a thermocouple at the center of one reacting pellet. The temperature recording showed that the maximum temperature difference between the bulk gas ( $T = 897^\circ\text{C}$ ) and pellet center was about  $5^\circ\text{C}$ , and the difference remained relatively constant. Since the accuracy of the thermocouples was  $\pm 6^\circ\text{C}$ , the actual temperature at the reacting interface—taken to be that at the pellet center—could have been as low as  $885^\circ\text{C}$ . At that temperature the equilibrium decomposition pressure of  $\text{SO}_2$  is 0.30 atm (22), and the value of  $P_{AC}^*$  based on a bulk gas temperature of  $897^\circ\text{C}$  for run TR-10 is 0.033 atm. Thus, the temperature difference within the pellet by itself would not account for the low-pressure values of apparent decomposition, although it tends to lower the equilibrium pressure.

A topochemical model that included a chemical reaction resistance was also tested on the experimental data. The model represented data rather well, but the chemical reaction accounted for 80% of the total resistance. Since the unreacted pellets had porosities ranging up to 47%, this is inconsistent with the observed topochemical behavior.

A comparison of the predicted with experimental conversion for runs TR-17 and TR-40 is presented in Figure 10. The predicted curve by the model was generated using  $P_{AC}^*$  from the least-squares correlation in Figure 9; the average deviation between the model and experimental conversion for all the runs was less than 3%. Some of the assumptions in the model were not realized experimentally. For example, the pellets actually had a slight eccentricity due to flaring of the dies and were not initially uniform and homogeneous, as indicated by preferential cracking at the equator.

The proposed model predicts that as the temperature is increased, the  $\text{SO}_2$  concentration in the exit gas becomes



**Figure 10.** Comparison of experimental data with proposed model for experiment TR-17 and TR-40

sufficient to permit the economical production of by-product sulfuric acid. If  $\text{MnSO}_4$  pellets are decomposed in a fixed bed under operating conditions comparable to those for TR-8 or at a nitrogen flow rate of 0.46 mol/min/mol of initial  $\text{MnSO}_4$ , the average concentration of  $\text{SO}_2$  in the exit gas based on the model for a 90% conversion of  $\text{MnSO}_4$  would be 5.1% at  $950^\circ\text{C}$  and 10.5% at  $1000^\circ\text{C}$ . The corresponding average rates of conversion are 2.5 and 5.8% per minute.

### Conclusions

The decomposition of  $\text{MnSO}_4$  pellets in nitrogen occurs in an approximately topochemical manner, producing  $\text{Mn}_3\text{O}_4$ ,  $\text{SO}_2$ , and  $\text{O}_2$ .

A topochemical model is proposed which satisfactorily predicts conversion in porous and dense pellets as a function of time.

The apparent decomposition pressure of  $\text{SO}_2$  based on the model is lower than the equilibrium value by approximately one order of magnitude.

Sintering occurred during the heating period and reduced the specific surface area of both porous and dense pellets by 75% to approximately  $0.7\text{ m}^2/\text{g}$ . Decomposition produces a porous product layer, and the specific surface area increases linearly with conversion.

Based on the proposed model, the  $\text{SO}_2$  concentration in the product gas would be in the 5–10% range when  $\text{MnSO}_4$  pellets are decomposed at  $950\text{--}1000^\circ\text{C}$  and a gas flow comparable to that used in this study.

### Acknowledgment

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### Nomenclature

- $A$  = diffusion resistance coefficient, min
- $B$  = film resistance coefficient, min
- $C_A$  = molar concentration of species  $A$ , mol/cc
- $C_{AC}^*$  = molar concentration of species  $A$ , mol/cc, at reacting interface
- $C_{AO}$  = molar concentration of species  $A$  in the bulk gas stream, mol/cc
- $C_{AS}$  = molar concentration of species  $A$  at the particle surface, mol/cc
- $C_{SD}$  = molar density of solid reactant, mol/cc
- $D_A$  = diffusion coefficient of species  $A$  in bulk gas,  $\text{cm}^2/\text{min}$
- $D_{eA}$  = effective diffusivity of species  $A$  through product layer,  $\text{cm}^2/\text{min}$
- $k_{MA}$  = mass transfer coefficient of species  $A$  through external film,  $\text{cm}/\text{min}$
- $P_{AC}^*$  = apparent decomposition pressure of species  $A$ , atm
- $r$  = radius, cm
- $r_c$  = radius of unreacted core, cm
- $r_o$  = radius of particle, cm

$T$  = temperature of bulk gas stream, °C  
 $t$  = length of reaction period, min  
 $v$  = volumetric flow rate of purge gas, cc/min  
 $W_A$  = rate of production of species  $A$  by reaction, mol/min  
 $z$  = fractional conversion, dimensionless

#### Greek Letters

$\alpha$  = averaging factor, dimensionless  
 $\epsilon_p$  = product layer void fraction, dimensionless  
 $\tau$  = tortuosity factor, dimensionless

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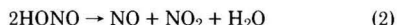
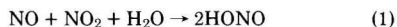
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## Kinetic Study of HONO Formation and Decay Reactions in Gaseous Mixtures of HONO, NO, NO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>

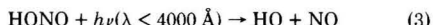
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Many of the mechanistic features of photochemical smog formation are reasonably well understood today (1-3). The chemical transformation of the atmospheric mixture of hydrocarbons, carbon monoxide, and the oxides of nitrogen to the notorious blend of irritants present in photochemical smog, ozone, peroxyacynitrates, acids, aldehydes, and the other oxidation products of the hydrocarbons is believed to occur by way of a series of chain reactions which involve various active free radical species as chain carriers. One of the most important of the active species is thought to be the HO-radical, and the nitrous acid molecule is one of several potential primary sources of this radical. Nitrous acid may build up in the atmosphere through the occurrence of Reactions 1 and 2:



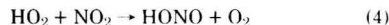
In turn, the photolysis of nitrous acid in sunlight may generate HO-radicals:



It is believed that the HO-radical reacts readily with the hydrocarbons, aldehydes, carbon monoxide, and other species to initiate the sequence of reactions which results in the oxidation of NO to NO<sub>2</sub> and the ultimate generation of ozone. A single primary HO-radical may initiate a sequence

of reactions involving many cycles which may lead to the oxidation of many molecules of hydrocarbon, CO, and NO. The oxidation of NO to NO<sub>2</sub> is a particularly significant event in that it controls the ozone level. Thus, the primary rate of generation of the HO-radical in a polluted atmosphere may influence strongly the concentration of ozone, the rate of the generation of the other manifestations of photochemical smog, and the severity of the smog episode.

There has been much speculation on the nature of the primary sources of the HO-radical in the sunlight-irradiated, polluted atmosphere, and it is not clear even today to what extent Reactions 1, 2, and 3 generate HO. Although Calvert and McQuigg concluded from smog simulation studies that the nitrous acid molecule is a major primary source of HO through nitrous acid photolysis in sunlight, in their reaction mechanism the major source of HONO was the reaction of HO<sub>2</sub> with NO<sub>2</sub> (3):



Although Reactions 1 and 2 may in theory also control the nitrous acid levels in the atmosphere, their importance in the atmosphere is uncertain, since the existing kinetic information on these reactions apparently does not apply to the homogeneous reactions.

In the first detailed study of the NO-NO<sub>2</sub>-H<sub>2</sub>O-HONO system, Wayne and Yost (4) followed NO<sub>2</sub> disappearance in mixtures rich in NO and H<sub>2</sub>O. The rates were reasonably

■ A kinetic study of the nitrous acid decay reaction,  $2\text{HONO} \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$  (2), and the formation reaction,  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HONO}$  (1), is made using essentially continuous FT-IR monitoring of the reactants and products in mixtures at the ppm level. The data suggest that the reactions are homogeneous for the conditions employed in this study. The results give:  $k_1 = (2.2 \pm 0.7) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$  and  $k_2 = (1.4 \pm 0.4) \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$  at 23 °C. The homogeneous generation of HONO may be important in power plant plumes and in auto exhaust gases during the early stages of the dilution of

these  $\text{NO}_x\text{-H}_2\text{O}$ -rich mixtures. Reactions 1 and 2 are a negligible source and sink of HONO in the atmosphere once the usual low ambient levels of NO and  $\text{NO}_2$  are achieved. These reactions may influence smog formation in urban atmospheres during the early morning hours when nitrous acid formation by alternative pathways is slow. For these conditions the sunlight photolysis of HONO may be the major source of HO-radicals which, in combination with hydrocarbons and their oxidation products, lead to  $\text{NO} \rightarrow \text{NO}_2$  conversion,  $\text{O}_3$  development, and other manifestations of photochemical smog.

fast. Leighton (5) derived from these data  $k_1 \approx 4.3 \times 10^{-6} \text{ ppm}^{-2} \text{ min}^{-1}$ , assuming that the kinetics of the reaction followed those of the elementary Reaction 1. However, in the subsequent study by Graham and Tyler (6), much smaller values for  $k_1$  were observed:  $k_1 = (1.2 \pm 0.6) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$ . As in the Wayne and Yost results, the kinetics at high water concentration did not follow the order with respect to the reactants predicted by the elementary step 1. The large difference between the rate constants observed in the two studies was attributed to the large difference in surface-to-volume ratio of the reaction vessels used (factor of 40). Hence, the observed reaction was thought to be controlled entirely by heterogeneous wall reactions. Recently, England and Corcoran (7) invoked the occurrence of Reactions 1 and 2 to rationalize their observed kinetic effects of water vapor on the rate of oxidation of NO to  $\text{NO}_2$  in the NO,  $\text{NO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$  system. They concluded from very indirect evidence that Reaction 1 did occur homogeneously at temperatures of 40 °C and above with  $k_1 = 1.5 \times 10^{-8} \text{ ppm}^{-2} \text{ min}^{-1}$ ; there was some indication of reaction heterogeneity for experiments near room temperature.

There are no previous quantitative estimates of  $k_2$ , but if the homogeneous Reaction 1 is slow, as the present evidence suggests, then one expects the reverse Reaction 2 to be slow as well, since the ratio of the two rate constants is equal to the equilibrium constant for the overall Reaction 1. Indeed, qualitative evidence for the slowness of Reaction 2 has been suggested in the studies of Asquith and Tyler (8), Nash (9), and Cox and coworkers (10). They have observed that HONO vapor is seemingly quite stable at concentrations well above its equilibrium level.

All present evidence suggests that the rate constants for the homogeneous Reactions 1 and 2 are small, and there is some question as to whether these reactions occur measurably at all in the gas phase. Demerjian et al. (1) also came to this conclusion in their review of the mechanism of photochemical smog formation. However, they noted that if HONO were present in an auto exhaust polluted atmosphere of typical composition at concentration near those for equilibrium with the NO,  $\text{NO}_2$ , and  $\text{H}_2\text{O}$  present in the early morning hours, then the predicted rate of conversion of NO to  $\text{NO}_2$  would be enhanced by a factor of two over that expected in the absence of HONO initially. Then it is clearly important to evaluate the rate constants for the homogeneous Reactions 1 and 2 to define the important initial rates of smog formation.

In all of the previous kinetic studies of the nitrous acid system, no direct measurement of nitrous acid itself was made. Previous workers depended upon either the determination of changes in visible light absorption due to the reactant  $\text{NO}_2$  alone, or on chemiluminescence detection of NO and  $\text{NO}_x$  coupled with the selective chemical removal of HONO vapors. Obviously, rate information based on the direct measurement of HONO vapor is necessary to test

the hypotheses formulated from the indirect experiments and to derive meaningful values of  $k_1$  and  $k_2$ . This has been possible in the work described here in which an FTS-infrared spectroscopic analysis of the NO,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , HONO system allowed essentially continuous monitoring of all the reactants and products. The relatively large reaction vessel employed in this work ensured a low surface-to-volume ratio and the minimization of wall effects. The cell size and the pressure of added nitrogen gas (700 torr) favored the homogeneous reaction paths for reactants. The multiple-pass White optical system allowed path lengths from 82 m to 1.5 km and measurements of very low reactant and product concentrations in the ppm range of major interest in the atmospheric reactions. We believe that this work provides the first direct measurement of the rate constants of the homogeneous Reactions 1 and 2. In terms of these results reasonable speculation is made about the potential role of these reactions in the atmosphere.

#### *Experimental Methods and Techniques*

**Reaction Vessel and Associated Optical System.** The reactions between NO,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , HONO mixtures were studied in a large stainless steel (Type 304) tank, 21 m in length and 76 cm in internal diameter. It could be evacuated using its associated high-vacuum booster pump (Kinney KMBD) to a pressure of a few microns in about 1 h when starting at atmospheric pressure within the cell. The cell housed a White optical system composed of three mirrors (20.5-m radius of curvature) with a base path length of 20.5 m. Two of the mirrors could be adjusted through external controls to allow alignment and variation in the number of optical traversals employed. Path lengths from 82 m up to 1.5 km could be employed. The cell was fitted with polished NaCl windows. Radiation from a Nernst glower was collimated and passed through a Michelson interferometer (Digilab 496). The output beam from the interferometer was focused into the absorption cell, and the exiting beam was collected by a copper-doped germanium photoconductor. This detector was operated at liquid helium temperature and had a useful spectral range which extended from 300 to  $3500 \text{ cm}^{-1}$ .

The Digilab 496 interferometer had a maximum retardation of 8 cm and a fixed scanning velocity of approximately  $1.5 \text{ mm s}^{-1}$ . The mirror motion and data acquisition were controlled by a helium-neon laser mounted on the interferometer. The system was designed to be able to interrogate the output from the detector every one-half of a laser interference fringe. For this study, however, we found a considerable saving in computational time could be achieved by recording data every other laser interference fringe. No loss of resolution or of signal-to-noise ratio was observed. All spectra recorded in this experiment were collected at  $0.5 \text{ cm}^{-1}$  resolution. Thus, 16,384 (16K) data points were collected and transformed.

The interferogram output from the detector, that is, the superposition of interference fringes from all of the wavelengths contained within the broad band source, was digitized by a 15-bit analog-to-digital converter. Phase correction of the interferogram was performed by a Nova 1200 minicomputer, and the computer then calculated the spectrum using boxcar apodization on the interferogram. The Nova 1200 computer was equipped with 4K of core and had a 128K fixed head disc and a 9-track, high-density magnetic tape unit as peripheral equipment.

**Gas Handling System.** The gas handling system was constructed from bulbs and tubing made of glass and stainless steel, and all stopcocks were made of Teflon. The introduction of measured quantities of the standard reactant gases, NO and NO<sub>2</sub>, was accomplished by filling calibrated 1-l. bulbs to some measured pressure and expanding these into the tank. About a 10<sup>4</sup> to 1 dilution of reactant concentrations occurred on expansion. Pressures were measured on one of three calibrated Wallace and Tiernan gauges (0–20, 0–50, 0–800 torr) appropriate for the measurement. The gauges were isolated from the sample by a quartz spiral gauge which was used as a null instrument.

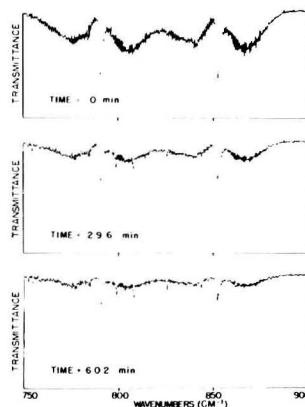
**Calibration of Reactant Gas Absorbance Data.** Although there are several infrared absorption bands characteristic of NO, NO<sub>2</sub>, and isomers of HONO in the mid-infrared region, all of them could not be employed for concentration-monitoring purposes since some were either overlapping those of atmospheric CO<sub>2</sub> and H<sub>2</sub>O or they mutually interfered. These interferences were reduced by obtaining all spectra with a spectral resolution of 0.5 cm<sup>-1</sup>. The unique absorption peaks which were employed in this work are: NO<sub>2</sub>, ν<sub>2</sub> band, Q-branch transition at 823 cm<sup>-1</sup>; NO, fundamental Q-branch at 1876 cm<sup>-1</sup>; *cis*-HONO, ν<sub>4</sub> band, Q-branch transition at 853 cm<sup>-1</sup>; *trans*-HONO, ν<sub>3</sub> band, Q-branch transition at 1264 cm<sup>-1</sup>. All absorbances were measured after adjusting the total pressure of the gaseous mixture to 700 torr with added high-purity nitrogen gas (Matheson Co.). The single-beam spectrometric system employed in this work required that a background spectrum of the detector profile and the cell filled with high-purity nitrogen (700 torr) be recorded first and then ratioed against the sample spectrum. Through the use of this procedure, the unwanted interferences from the absorption due to atmospheric water vapor and CO<sub>2</sub> were minimized.

Calibration was carried out in three cells of path length, 7.5 cm, 39.5 cm, and 20.5 m, respectively. In the case of the reactant nitric oxide (Matheson Co., 99% NO), a measured pressure of the gas was introduced into one of the three cells; then the cell was pressurized to 700 torr with high-purity nitrogen. The absorbance at the peak of the distinctive Q-branch of NO at 1876 cm<sup>-1</sup> was then measured. Plots of absorbance vs. path length-concentration product were linear over the wide range of concentrations investigated here. The calibration procedure with nitrogen dioxide gas was necessarily more complicated because of the dynamic equilibrium, 2NO<sub>2</sub> ⇌ N<sub>2</sub>O<sub>4</sub>. The NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub> sample (Matheson Co., 99.5% N<sub>x</sub>O<sub>2x</sub>) was purified further before use by condensation at liquid N<sub>2</sub> temperature and by degassing to remove volatile impurities (NO, N<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, etc.). The degassed sample was then allowed to expand into the desired cell for calibration, and the pressure of the NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub> mixture was measured. The corresponding partial pressure of NO<sub>2</sub> was calculated using the known equilibrium constant for the temperature employed (23 °C). Again, the cell was pressurized to 700 torr with added high-purity nitrogen gas. The absorbance of the NO<sub>2</sub> was measured at the peak of the characteristic Q-branch transition at 823 cm<sup>-1</sup>.

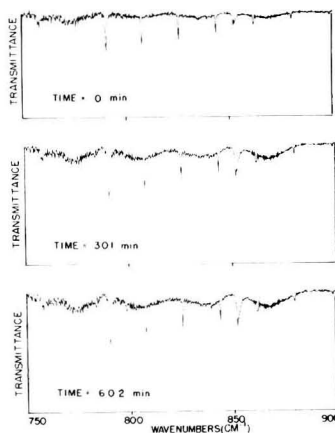
The calibration of nitrous acid vapor spectra also re-

quired the use of indirect methods. One cannot prepare pure samples of HONO vapor at any desired pressure because it is relatively unstable at concentrations above those corresponding to its rather low equilibrium pressure in NO, NO<sub>2</sub>, H<sub>2</sub>O mixtures. Thus, we have made measurements on equilibrium mixtures at 23 °C to establish our HONO calibrations. We have calculated the extinction coefficient of the HONO isomers using the known equilibrium ratio of [*trans*-HONO]/[*cis*-HONO] ≈ 2.29, and K<sub>1</sub> = 1.51 × 10<sup>-6</sup> ppm<sup>-1</sup> at 23 °C [derived from the least-squares fit of all published data (4, 11, 12)], together with measured absorbances of *trans*-HONO and *cis*-HONO, NO, and NO<sub>2</sub> in mixtures of known pressure of water vapor. The extinction coefficients {ε = [ln(I<sub>0</sub>/I)]/pl} which we have determined and employed in this study (spectral resolution of 0.5 cm<sup>-1</sup>, temp, 23 °C) are as follows: NO (1876 cm<sup>-1</sup>), ε = 0.513 ± 0.006 torr<sup>-1</sup> m<sup>-1</sup>; NO<sub>2</sub> (823 cm<sup>-1</sup>), 0.0807 ± 0.0012 torr<sup>-1</sup> m<sup>-1</sup>; *cis*-HONO (853 cm<sup>-1</sup>), 9.36 ± 0.94 torr<sup>-1</sup> m<sup>-1</sup>; *trans*-HONO (1264 cm<sup>-1</sup>), 5.20 ± 0.52 torr<sup>-1</sup> m<sup>-1</sup>.

In kinetic studies of the HONO decomposition reaction, samples of nitrous acid much in excess of the equilibrium pressure were introduced into the large reaction cell following a procedure modified somewhat from that used in



**Figure 1a.** Absorption spectrum of reacting mixture of HONO, NO, NO<sub>2</sub>, and H<sub>2</sub>O; note decrease in ν<sub>4</sub> bands of *trans*-HONO (791 cm<sup>-1</sup>) and *cis*-HONO (853 cm<sup>-1</sup>) and buildup of NO<sub>2</sub> transitions as time progresses in originally HONO-rich mixture



**Figure 1b.** Absorption spectrum of reacting mixture of HONO, NO, NO<sub>2</sub>, and H<sub>2</sub>O; note growth of HONO peaks as time progresses in originally HONO-poor mixture



the studies of Nash (9) and Cox and coworkers (10). Three methods were attempted: Dilute  $\text{H}_2\text{SO}_4$  was added to dilute  $\text{NaNO}_2$  solution, dilute  $\text{H}_2\text{SO}_4$  was added to solid  $\text{NaNO}_2$ , and dilute  $\text{NaNO}_2$  was added to dilute  $\text{H}_2\text{SO}_4$  solution. The third method proved to be the best for our conditions in that it gave the maximum ratio of  $[\text{HONO}]/([\text{NO}] + [\text{NO}_2])$ . A dilute  $\text{NaNO}_2$  solution ( $\sim 0.3 \text{ M}$ ) contained in a dropping funnel was added slowly to a dilute  $\text{H}_2\text{SO}_4$  solution ( $\sim 2.5 \text{ M}$ ) in a 3-neck flask.  $\text{N}_2$  gas was allowed to flow into the vessel through one neck of the flask and was directed upward by the inlet tube at the solution-gas interface. The vapors containing HONO were swept into the cell by the flow of  $\text{N}_2$  gas which was carried through a tube attached to the second neck of the flask. The entire apparatus was flushed with nitrogen before use. A trap containing concentrated  $\text{NaOH}$  solution was attached to the third neck of the flask and prevented the entry of air during the preparation and served as a sink for the excess of reactants after HONO preparation.

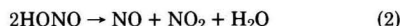
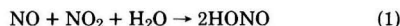
**Experimental Procedure in Kinetic Runs.** *HONO Decomposition Reaction.* Before each run a carefully measured quantity of liquid water was allowed to evaporate and enter the evacuated reaction cell. The transfer was facilitated through the use of a nitrogen carrier gas. Water sufficient to provide in the tank 190–4200 ppm in  $\text{H}_2\text{O}$  concentration was used so that  $\text{H}_2\text{O}$  which was formed in the reactions was always a negligible fraction of the total water present. Then the cell was filled to a pressure of 400–500 torr of high-purity nitrogen gas. During a 5-min period the HONO was added by means of the nitrogen carrier as described previously. During a 5–10-min period a very fast flow of nitrogen gas was used to turbulently mix the gaseous reactants and to achieve a final pressure of 700 torr. Spectra were taken (2-min collection period) at regular time intervals (4–10 min), stored on tape, and the absorption spectra were computed automatically by ratioing against the previously recorded background cell spectrum. In these runs a 246-m path was normally employed. Typical spectra for several time periods can be seen in Figure 1a. The absorptions due to the vibrational transitions of *trans*-HONO ( $791 \text{ cm}^{-1}$ ) and *cis*-HONO ( $853 \text{ cm}^{-1}$ ) decrease as the decomposition of HONO occurs, and absorptions due to  $\text{NO}_2$  transitions appear at  $823 \text{ cm}^{-1}$  and at several other wavelengths between the two HONO  $\nu_4$  bands. One  $\text{NO}_2$  absorption peak overlaps that of *trans*-HONO so that the  $791\text{-cm}^{-1}$  band was not used as a quantitative measure of *trans*-HONO. The  $1264\text{-cm}^{-1}$  absorption band of this isomer showed no such interference and was used for quantitative *trans*-HONO estimates.

*HONO Formation Reactions.* Water was introduced to

the evacuated cell as before, then  $\text{NO}$  gas, followed by  $\text{N}_2$  gas to bring the total pressure to 400–500 torr.  $\text{NO}_2$  was then added, and the cell pressurized to 700 torr with a very rapid flow of nitrogen gas which ensured turbulent mixing of the reactants. Spectra were recorded as before, but in this case, a pathlength of 492 m was employed to enhance the absorption of the smaller HONO concentrations in these mixtures. Absorbances of  $\text{NO}$ ,  $\text{NO}_2$ , *cis*-HONO, and *trans*-HONO were then calculated from plots of the ratioed absorption spectra for each measured time period. Typical absorbance changes in one spectral region can be seen in Figure 1b. The absorbance spikes due to the  $\text{NO}_2$  Q-branch transition at  $823 \text{ cm}^{-1}$  and several other spectral positions occur as prominent features while growth of the *trans*-HONO and *cis*-HONO bands is observed at the longer run times.

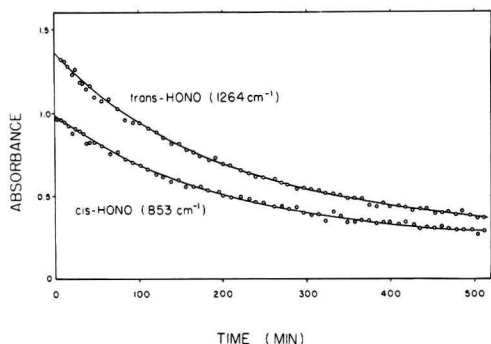
### Experimental Results and Discussion

**Kinetics of HONO Decomposition in Gas Phase.** In the present work we have introduced gaseous HONO into the reaction cell at concentrations well in excess of its equilibrium values and observed by infrared Fourier transform spectroscopy the kinetics of its return to equilibrium with  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{H}_2\text{O}$  vapors, presumably through the occurrence of Reactions 1 and 2:

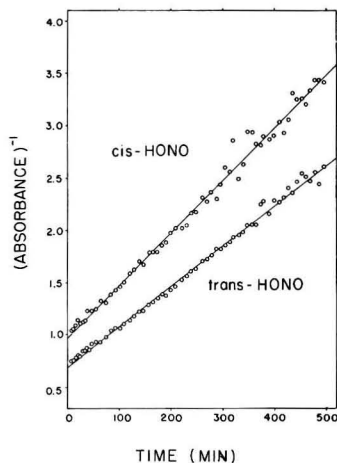


The data given in Figure 2 show the time dependence of the absorbance measured at the maximum in the Q-branch of the *trans*-HONO  $\nu_3$  band at  $1264 \text{ cm}^{-1}$  and the *cis*-HONO  $\nu_4$  band at  $853 \text{ cm}^{-1}$ . Note that the two isomers decay essentially in tandem, and the rate is very slow; for the concentrations employed here, somewhat less than one-half of the HONO has disappeared in about 200 min. The ratio of the two absorbances ( $a_{\text{cis}}/a_{\text{trans}}$ ) stays nearly constant although it may increase very slightly with time. For example, in the data shown in Figure 2, the linear least-squares fit of the dependence of the absorbance ratio on time follows the equation,  $(a_{\text{cis}}/a_{\text{trans}}) = 0.724 \pm 0.012 + (7.2 \pm 3.8) \times 10^{-5} t(\text{min})$ , through 575 min of the reaction. The absorbance ratios noted during the reaction appear to be somewhat lower than those observed for mixtures near equilibrium at room temperature. The average of 172 different determinations in runs with temperatures from 21.4 to  $30.0 \text{ }^\circ\text{C}$ , gave:  $a_{\text{cis}}/a_{\text{trans}} = 0.790 \pm 0.040$ ; no significant trend with temperature over this relatively small temperature interval was obtained. Thus, there is some suggestion that in the decomposition Reaction 2, the *cis*-HONO isomer is depleted more rapidly than the *trans*-HONO isomer. However, our data provide no convincing evidence of this; in fact, one would not expect such an effect since the relatively small barrier to isomerization of the HONO isomers,  $8.7 \pm 1 \text{ kcal/mol}$  (13), should allow equilibration of the isomers to occur very rapidly even if one of the isomers were removed preferentially. Thus, if the isomerization reaction is in the first-order region at 700 torr and it has a "normal" preexponential factor ( $\sim 10^{13} \text{ s}^{-1}$ ), then  $\tau_{1/2} \approx 1.8 \times 10^{-7} \text{ s}$  at  $23 \text{ }^\circ\text{C}$ .

A clue as to the kinetics of the decay of nitrous acid can be obtained from the plot of the reciprocal of the absorbances of the two isomers vs. time. This may be seen in Figure 3 for the data from the early part of a typical HONO decomposition experiment. The linear form of the plots suggests strongly that the rate-determining step in the HONO decomposition is second order in nitrous acid. Since equilibration between the *cis*-HONO and *trans*-HONO forms is very rapid, we cannot determine in these experi-



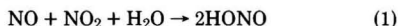
**Figure 2.** Absorbance vs. time plot for *trans*-HONO ( $1264 \text{ cm}^{-1}$ ) and *cis*-HONO ( $853 \text{ cm}^{-1}$ ) in HONO- $\text{NO}$ - $\text{NO}_2$ - $\text{H}_2\text{O}$  mixture originally rich in HONO



**Figure 3.** Plot of reciprocal of absorbance of *trans*-HONO (1264  $\text{cm}^{-1}$ ) and *cis*-HONO (853  $\text{cm}^{-1}$ ) vs. time for HONO-NO-NO<sub>2</sub>-H<sub>2</sub>O mixture originally rich in HONO

ments the rate constants for specific pairs of reactants: cis-cis, cis-trans, and trans-trans. However, we may use the data of Figure 3 to derive an estimate of the second-order rate constant for total HONO loss. The least-squares slopes of the lines for the *cis*- and *trans*-HONO data,  $(5.03 \pm 0.04) \times 10^{-3}$  and  $(3.86 \pm 0.08) \times 10^{-3} \text{ min}^{-1}$ , are equal in theory to  $2k_{\text{cis}}/\epsilon_{\text{cis}l}$  and  $2k_{\text{trans}}/\epsilon_{\text{trans}l}$ , respectively. Here,  $k_{\text{cis}}$  and  $k_{\text{trans}}$  refer to the apparent second-order rate constants for the hypothetical reactions involving only cis-cis and trans-trans pairs, respectively. The true second-order rate constant  $k_2$  for the total nitrous acid decay is related to  $k_{\text{cis}}$  and  $k_{\text{trans}}$  by:  $k_2 = [(k_{\text{cis}}/R) + k_{\text{trans}}][R/(1+R)]^2$ , where  $R$  is the equilibrium ratio of  $[\textit{trans}\text{-HONO}]/[\textit{cis}\text{-HONO}] \approx 2.29$  (23 °C). Thus, for the data given in Figure 3,  $k_2 = (1.28 \pm 0.06) \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$ .

As the reaction proceeds to much longer times, the rate of nitrous acid loss decreases until equilibrium levels of HONO, NO<sub>2</sub>, NO, and H<sub>2</sub>O are achieved. This may be noted in the extended run shown in Figure 4. The total nitrous acid concentration is plotted for a run followed over a period of 28 h. Obviously, a nitrous acid forming reaction becomes important at long times. It is reasonable to assume this effect to be the result of the occurrence of Reaction 1, the reverse of Reaction 2.



If Reactions 1 and 2 are truly elementary reactions and they are the only reactions involving HONO in our system, then the simple rate law which should describe HONO decay over the entire time scale is Equation 5:

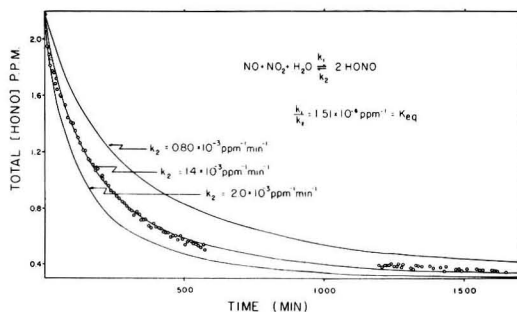
$$-\frac{dP_{\text{HONO}}}{dt} = (P_{\text{HONO}})^2 2k_2 - P_{\text{NO}}P_{\text{NO}_2}P_{\text{H}_2\text{O}} 2k_1 \quad (5)$$

For the conditions employed in our study, the water vapor is present in large excess so that  $P_{\text{H}_2\text{O}}$  remains essentially constant throughout a given experiment. The integrated form of the rate Equation 5 for the conditions employed in this work may be shown to be given by Equation 6:

$$(P_{\text{HONO}})_t = (P_{\text{HONO}})_0 - \frac{(b + \sqrt{-q})(1 - e^{t\sqrt{-q}})}{2c \left[ e^{t\sqrt{-q}} - \frac{b + \sqrt{-q}}{b - \sqrt{-q}} \right]} \quad (6)$$

where

$$a = (P_{\text{HONO}})_0^2 2k_2 - (P_{\text{H}_2\text{O}})_0(P_{\text{NO}_2})_0(P_{\text{NO}})_0 2k_1$$



**Figure 4.** Plot of total HONO concentration vs. time for extended run of 1648-min duration using initially HONO-rich mixture; initial concentrations, ppm: HONO, 2.14; NO, 2.37; NO<sub>2</sub>, 3.53; H<sub>2</sub>O, 4200; temperature, 23 °C; curves calculated using Equation 6 and rate constant values indicated on figure

$$b = -\{4k_2(P_{\text{HONO}})_0 + (P_{\text{H}_2\text{O}})_0[(P_{\text{NO}_2})_0 + (P_{\text{NO}})_0]k_1\}$$

$$c = 2k_2 - (P_{\text{H}_2\text{O}})_0k_1/2$$

$$q = 4ac - b^2$$

and  $P_{\text{HONO}}$  refers to the total pressure of nitrous acid present,  $P_{\text{trans-HONO}} + P_{\text{cis-HONO}}$ . Subscripts of  $t$  and  $0$  on the reactant pressures refer to time  $t$  and time  $0$ , respectively.

A test of the fit of the data of an extended run of 1648-min duration to the form of Relation 6 is shown in Figure 4. In attempting to fit the theoretical time dependence curve to these data and derive rate constant information, we varied the value of  $k_2$  chosen for the calculation, but then the choice of  $k_1$  was fixed through the known equilibrium constant and its relation to  $k_1$  and  $k_2$ :  $k_1 = k_2K_1$ ;  $K_1$  corresponds to the equilibrium:  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HONO}$ . The sensitivity of the fit of the theoretical curve to the choice of  $k_2$  is seen in Figure 4. For the particular conditions employed in this run, a choice of  $k_2 = 1.4 \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$ , and hence  $k_1 = (1.51 \times 10^{-6})(1.4 \times 10^{-3}) = 2.1 \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$ , fits well the data through the Equation 6 over the entire range of the experiment. This choice of  $k_2$  also is in good accord with that derived from the  $1/a_{\text{cis}}$  and  $1/a_{\text{trans}}$  vs. time plots of the initial rate data for this experiment as outlined previously:  $k_2 = (1.3 \pm 0.1) \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$ . Similar kinetic constants were obtained from many other experiments in which the initial pressures of HONO, NO<sub>2</sub>, NO, and H<sub>2</sub>O were varied; the data were fitted again as outlined. The estimates of  $k_2$  and  $k_1$  derived from these experiments are summarized in Table I. There is a reasonably good agreement between the estimated constants from different experiments. Note particularly that the rate constant estimates obtained from runs at 20 and 300 torr of added nitrogen gas pressure are within the experimental error, the same as those found in the usual experiments which were pressurized to 700 torr of nitrogen gas. This supports the conclusion that the rate of HONO disappearance in these runs is controlled by homogeneous reactions and is not influenced significantly by reactions which are diffusion controlled and occur at the cell wall.

This study provides the first measurements of the HONO decomposition reaction. The data seem to suggest that HONO decay occurs by an elementary reaction of the stoichiometry required by Reaction 2 with a rate constant  $k_2 = (1.4 \pm 0.4) \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$  at  $23 \pm 1$  °C. The fit of these rate data to the decay at long times gives  $k_1 = (2.1 \pm 0.7) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$  at  $23 \pm 1$  °C.

**Kinetics of HONO Formation Reaction in Gas Phase.** Evidence of the kinetics which controls Reaction 1,

**Table I. Summary of Rate Constant Estimates<sup>a</sup> for Reactions: NO + NO<sub>2</sub> + H<sub>2</sub>O → 2HONO (Reaction 1) and 2HONO → NO + NO<sub>2</sub> + H<sub>2</sub>O (Reaction 2)**

Initial concentrations, ppm <sup>b</sup>						
[NO]	[NO <sub>2</sub> ]	[H <sub>2</sub> O]	[HONO]	P <sub>N<sub>2</sub></sub> , torr	k <sub>2</sub> , ppm <sup>-1</sup> min <sup>-1</sup>	k <sub>1</sub> , ppm <sup>-2</sup> min <sup>-1</sup>
2HONO → NO + NO <sub>2</sub> + H <sub>2</sub> O experiments						
5.42	7.81	560	6.73	700	1.6 × 10 <sup>-3</sup>	2.4 × 10 <sup>-9</sup>
5.65	7.01	1120	6.04	700	1.6 × 10 <sup>-3</sup>	2.4 × 10 <sup>-9</sup>
4.64	5.60	2240	5.21	700	1.4 × 10 <sup>-3</sup>	2.1 × 10 <sup>-9</sup>
5.18	4.89	2800	3.95	700	0.90 × 10 <sup>-3</sup>	1.4 × 10 <sup>-9</sup>
2.37	3.53	4200	2.14	700	1.4 × 10 <sup>-3</sup>	2.1 × 10 <sup>-9</sup>
4.23	8.50	190	9.01	300	1.5 × 10 <sup>-3 c</sup>	2.3 × 10 <sup>-9 c</sup>
1.91	10.7	190	4.77	20	2.3 × 10 <sup>-3 c</sup>	3.5 × 10 <sup>-9 c</sup>
NO + NO <sub>2</sub> + H <sub>2</sub> O → 2HONO experiments						
15.8	8.16	1400	0.130	700	0.80 × 10 <sup>-3</sup>	1.2 × 10 <sup>-9</sup>
10.6	9.72	2240	0.141	700	1.4 × 10 <sup>-3</sup>	2.1 × 10 <sup>-9</sup>
Best estimates					(1.4 ± 0.4) × 10 <sup>-3</sup>	(2.2 ± 0.7) × 10 <sup>-9</sup>

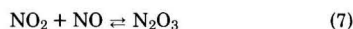
<sup>a</sup> Temperature in all runs, 23 ± 1 °C. <sup>b</sup> The unit ppm used here is defined as [pressure(torr)/760] × 10<sup>6</sup> at 23 °C. <sup>c</sup> Calculated assuming there is no pressure dependence in the extinction coefficient of the Q-branch of the vibrational bands used for concentration estimation; this appears to be a good approximation from a limited study of the effect of pressure on the absorbance of the species involved here.

H<sub>2</sub>O + NO + NO<sub>2</sub> → 2HONO, is derived from the dependence of the rate of HONO decay on the reactant pressures in experiments over long times during which equilibrium is approached; the values of *k*<sub>1</sub> obtained in this manner were described in the previous section. We attempted to determine *k*<sub>1</sub> in more direct experiments in which NO, NO<sub>2</sub>, and H<sub>2</sub>O were added to the cell and the rate of HONO formation was observed. This reaction turned out to be much more difficult to observe quantitatively in our apparatus than the study of Reaction 2. The difficulty arose primarily in making up the original NO<sub>2</sub>, NO, and H<sub>2</sub>O dilute mixture in the cell without allowing the reactants to encounter one another prematurely at elevated concentrations. In general, we were successful in preparing mixtures which were only a factor of two or three from the equilibrium level of HONO; therefore, the data are less useful for estimating *k*<sub>1</sub> values than we had hoped. However, in treating the data from such experiments, the concentration vs. time profiles for HONO formation were again matched by making appropriate choices in *k*<sub>1</sub> using the rate equation given by Relation 6. In this case, *k*<sub>2</sub> was adjusted so that *k*<sub>2</sub> = *k*<sub>1</sub>/*K*<sub>1</sub>. The estimated rate constants from two such runs are given in Table I. Although our precision is low for these experiments, we conclude that the same rate constants derived in the study of Reaction 2 fit the reverse reaction kinetics reasonably well; the best estimate from all of the data gives *k*<sub>1</sub> = (2.2 ± 0.7) × 10<sup>-9</sup> ppm<sup>-2</sup> min<sup>-1</sup>. Reaction 1 has been studied previously, and the results of these studies should be reviewed here in light of our new findings.

The Graham and Tyler (6) kinetic data for Reaction 1 were derived from experiments over a wide range of reactant concentrations: *P*<sub>NO</sub> = 4.3–200 torr; *P*<sub>NO<sub>2</sub></sub> = 1.7–7.5 torr; *P*<sub>H<sub>2</sub>O</sub> = 4.7–14 torr. Although these results seem to show an enhanced rate of reaction for runs at *P*<sub>H<sub>2</sub>O</sub> > 9 torr, which suggests an order for H<sub>2</sub>O higher than one, the calculated third-order rate constants for Reaction 1 for *P*<sub>H<sub>2</sub>O</sub> < 9 torr appear to be reasonably constant over the wide range of reactant concentrations employed. Indeed, the average value of the third-order rate constant *k*<sub>1</sub> derived from the Graham and Tyler data, *k*<sub>1</sub> = (1.2 ± 0.6) × 10<sup>-9</sup> ppm<sup>-2</sup> min<sup>-1</sup>, is equal within the experimental uncertainties of the two very different measurements to that observed here: *k*<sub>1</sub> = (2.2 ± 0.7) × 10<sup>-9</sup> ppm<sup>-2</sup> min<sup>-1</sup>. In view of the facts that the surface-to-volume ratio of the reaction vessel in our study was much lower than that of Graham

and Tyler (0.052 compared to 1 cm<sup>-1</sup>) and the concentration ranges of all the reactants were several orders of magnitude lower (10<sup>-3</sup>–10<sup>-5</sup>) in our work, the degree of agreement observed from the two very different systems provides strong evidence that the rate constant observed here is indeed that for a homogeneous reaction. It seems likely to us that the data of Graham and Tyler also may apply to the homogeneous system, at least at the lower H<sub>2</sub>O pressures.

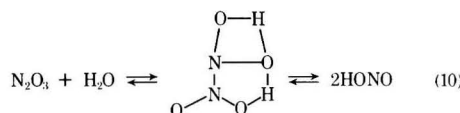
**Mechanism of Nitrous Acid Formation and Decay Reactions.** In most previous work the mechanism of the nitrous acid formation has been considered to involve the following reactions:



Since the equilibrium (Reaction 7) is established rather rapidly (14–16), the occurrence of this mechanism would be consistent with the overall kinetics of nitrous acid formation observed here and in the work of Graham and Tyler. The rate of nitrous acid formation would be given by:

$$\frac{dP_{\text{HONO}}}{dt} = 2 k_8 K_7 P_{\text{NO}} P_{\text{NO}_2} P_{\text{H}_2\text{O}} \quad (9)$$

The value for *K*<sub>7</sub> is 5.2 × 10<sup>-7</sup> ppm<sup>-1</sup> at 25 °C (17). Thus, in terms of Reaction 7, Reaction 8 for HONO formation, and the present value for *k*<sub>1</sub>, *k*<sub>8</sub> = 4.2 × 10<sup>-3</sup> ppm<sup>-1</sup> min<sup>-1</sup>. This hypothetical route of reaction would in theory involve a rather complex transition state:



The preexponential *A*-factor for such a highly ordered transition state should be much lower than the bimolecular collision number. If the activation energy for Reaction 8 is near zero ( $\Delta H_{298} = 0.6$  kcal), then, in a sense, the N<sub>2</sub>O<sub>3</sub> involvement could be justified in terms of the present kinetic data. However, if one considers the reverse Reaction 2 and the requirement that the same transition state be involved as in Reaction 1, then the kinetic data definitely favor an alternative reaction scheme.

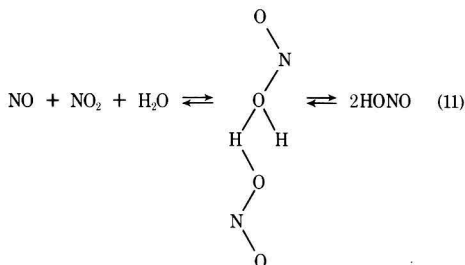
**Table II. Equilibrium Data Derived from Temperature Drift Experiments:  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HONO}$  (Reaction 1)**

Conditions at  $d[\text{HONO}]/dt = 0$ ; concn, ppm<sup>a</sup>

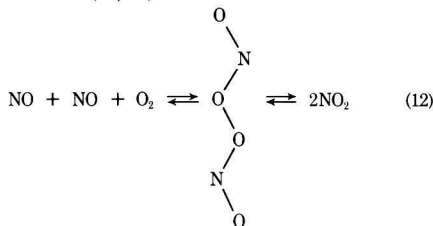
Temp, K	[NO]	[NO <sub>2</sub> ]	[HONO]	[H <sub>2</sub> O]	$K_1, \text{atm}^{-1}$
295.3	9.26	14.5	0.539	1323	1.64
295.6	9.26	14.5	0.542	1323	1.65
295.6	2.74	7.00	0.350	4200	1.52
296.9	14.0	23.3	0.634	915	1.35
297.0	2.57	6.21	0.308	4225	1.41
297.9	9.30	14.54	0.470	1335	1.22
299.7	9.49	12.6	0.405	921	1.49
300.1	7.96	14.6	0.406	1301	1.09
303.0	7.48	15.2	0.347	1314	0.806
303.1	9.28	12.7	0.355	931	1.15

<sup>a</sup> The unit ppm used here is defined as  $[\text{pressure (torr)}/760] \times 10^6$  at the temperature shown for the particular experiments.

A seemingly more realistic mechanism for Reactions 1 and 2 involves a much simpler transition state:



The transition state involves formation of only one common H-atom bond between the reactants. Note the similarity between this reaction pathway and that proposed for the ternary reaction of NO oxidation and its reverse bimolecular reaction (18, 19):

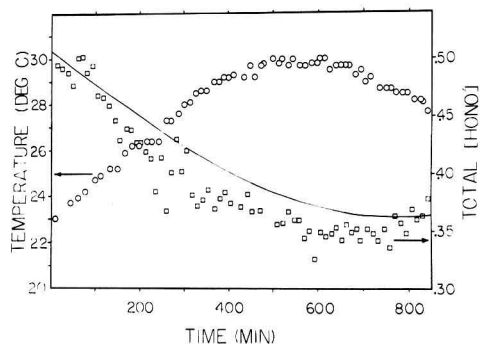


The entropy of activation for Reaction 12 should be very similar to that for 11; hence, one might expect very similar preexponential factors for the two reactions. We do not know the activation energy of Reaction 1; therefore, we cannot estimate directly the experimental  $A$ -factor for this reaction;  $\Delta H_{298}$  for the reaction is about  $-9.5$  kcal. The measured rate constant for the forward Reaction 12,  $k_{12} = 1.43 \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$  (19), is very nearly equal to that observed here for Reaction 1;  $k_1 = (2.2 \pm 0.7) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$ . The similarity in transition states of Reactions 11 and 12, and hence preexponential factors, coupled with the similarity in rate constants and the experimental value of  $E_{12} \leq 0$ , leads one to conclude that  $E_1$  may be near zero as well. Accepting this choice, we may estimate from the value of  $\Delta H_1$  that  $E_2 \approx 9.5$  kcal; then from the measured value of  $k_2$ ,  $A_2 \approx 1.3 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ . The reasonableness of this choice of rate parameters is seen by comparison of the analogous reverse reactions of 11 and 12. In theory these reactions have very similar transition states

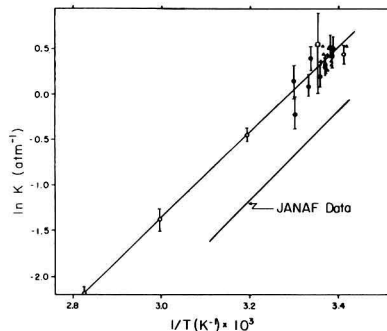
and reactants; hence, we would anticipate that  $\Delta S^\ddagger$  and the  $A$ -factors for these reactions would be similar. Indeed, the experimental value of  $A_{-12} \approx 1.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$  (20) is in good accord with  $A_2 \approx 1.3 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$  suggested here.

All of the present data seem consistent with the simple mechanism outlined in Reaction 11 as a description of Reactions 1 and 2. The involvement of  $\text{N}_2\text{O}_3$  as an intermediate in the reaction seems unnecessary and unwarranted. The activation energy assignments made here may be tested with the limited temperature variation studies described in the following section.

**Equilibrium Studies and Temperature Dependence of Nitrous Acid Formation and Decay Reactions.** The effect of temperature on the rate of the HONO decay reaction could not be determined accurately with the large reaction vessel employed in this work since the tank had no special temperature control other than the air conditioning system for the laboratory in which it was housed. We did utilize this air control system in a series of runs designed to determine the equilibrium constant and rates of [HONO] change with temperature. Typical data for one of the mixtures studied are shown in Figure 5. The tank contained a mixture of NO, NO<sub>2</sub>, H<sub>2</sub>O, and HONO at equilibrium. The air conditioner was turned off in the morning hours, and the temperatures of the room and the tank housed therein



**Figure 5.** [HONO] (squares) and temperature (circles) within cell vs. time for HONO-NO-NO<sub>2</sub>-H<sub>2</sub>O mixture near equilibrium; typical data used to determine equilibrium constant for reaction,  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HONO}$ , and to provide qualitative test of temperature dependence to rate constants; see text



**Figure 6.** Plot of  $\ln K(\text{atm}^{-1})$  vs.  $1/T$  for literature data and present results for equilibrium,  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HONO}$ . Open circles, Ashmore and Tyler (12); square, average of data of Wayne and Yost (4); triangles, Waldorf and Babb (17); closed circles, this work; locus of JANAF-suggested values and least-squares fit of published equilibrium data, excluding those of present study, are shown

were allowed to rise during the day as the outside temperature climbed. The infrared spectra of the reactants and the temperature at the center of the tank were monitored at regular intervals. Note in Figure 5 that the HONO concentration vs. time plot (squares) mirrors the temperature-time variation (circles) within the cell; the HONO is depleted as the temperature rises and the equilibrium is disturbed. The rate of Reaction 2 increases faster than that of 1 with rise in temperature since  $\Delta H_1 \approx E_2 - E_1 \approx 9.5$  kcal. After the system had reached a temperature desired, the air conditioner was turned on, and the temperatures of the room and the cell were lowered while the monitoring continued. At about 626 min after the start of the experiment shown in Figure 5, the rate of change of nitrous acid became equal to zero; of course, at this time the values of  $P_{NO}$ ,  $P_{NO_2}$ ,  $P_{H_2O}$ ,  $P_{cis-HONO}$ , and  $P_{trans-HONO}$  corresponded to those for equilibrium at the particular cell temperature recorded for this time (29.8 °C in Figure 5).

Thus, from a series of such temperature drift data in which the  $d[HONO]/dt = 0$  was caused to occur at a series of different temperatures, we have been able to estimate the equilibrium constant for the NO, NO<sub>2</sub>, H<sub>2</sub>O system at several temperatures. These data are given in Table II and refer to the equilibrium,  $NO + NO_2 + H_2O \rightleftharpoons 2HONO$ . The data are reasonably consistent with equilibrium data derived from previous indirect measurements in which only NO<sub>2</sub> concentrations were monitored and a mass balance assumption was made. All of the data are plotted in Figure 6.

A least-squares fit of the previous equilibrium data for the HONO, H<sub>2</sub>O, NO, NO<sub>2</sub> system (10–12) gives the equation,  $\ln K(\text{atm}^{-1}) = -15.56 \pm 0.62 + (4.73 \pm 0.19) \times 10^3/T$ ; the average of the data of Wayne and Yost was included only as a single point in this treatment since the scatter is greatest for this early work. For this relation we would estimate  $\Delta H_{298} = 9.4 \pm 0.4$  kcal. Our present data over the very limited temperature range available to us give  $\ln K(\text{atm}^{-1}) = -15.09 \pm 3.45 + (4.59 \pm 1.03) \times 10^3/T$  and  $\Delta H_{298} \approx 9.1 \pm 2.0$  kcal. Within the very limited accuracy of our data, the agreement of all the data is considered to be satisfactory.

The temperature drift data can be used to test approximately the suggested temperature dependence of the rate constants,  $k_1$  and  $k_2$ . The differential Equation 5 was employed in a computer calculation with not only the reactant concentrations but the rate constants themselves being time-dependent functions related to the temperature changes with time. For one case, shown in Figure 5 by the solid curve, we have tried to match the rate of change of [HONO] at the early times; we have taken  $k_2(\text{ppm}^{-2} \text{min}^{-1}) = 6.7 \times 10^4 e^{-10(\text{kcal/mol})/RT}$  with  $k_1 = K_1 k_2$ . The data appear to be qualitatively consistent with the expectations of Equation 5 and  $E_1 \approx 0$ ,  $E_2 \approx 10$  kcal/mole. The temperature drift data are not good enough to attempt further refinement of values of  $E_1$  and  $E_2$  since the nonuniformity of the cell temperature along its length could not be avoided completely. However, we may conclude that these data are consistent with a low activation energy for Reac-

**Table III. Theoretical Development of HONO as Function of Time for Mixtures of NO, NO<sub>2</sub>, and H<sub>2</sub>O for Compositions Typical of Stack Gas Emissions and Ambient Conditions**

Initial concn, ppm		Rel humidity, % (25 °C)	[NO <sub>2</sub> ]/[NO]	Concentration of HONO at time shown, ppm <sup>a</sup>										Equilibrium
[NO]	[NO <sub>2</sub> ]			1 s	10 s	30 s	5 min	10 min	1 h	6 h	60 h			
500	50	100	0.10	0.0574	0.572	1.70	14.6	22.9	29.1	29.1	29.1	29.1	29.1	
100	15	100	0.15	0.00345	0.0345	0.103	1.008	1.95	6.67	7.33	7.33	7.33	7.33	
50	9	100	0.18	0.00103	0.0103	0.0310	0.306	0.604	2.81	4.06	4.06	4.06	4.06	
10	2	100	0.20	$4.6 \times 10^{-5}$	$4.6 \times 10^{-4}$	$1.4 \times 10^{-3}$	$1.4 \times 10^{-2}$	$2.7 \times 10^{-2}$	0.160	0.677	0.860	0.860	0.860	
5	1.15	100	0.23	$1.3 \times 10^{-5}$	$1.3 \times 10^{-4}$	$4.0 \times 10^{-4}$	$4.0 \times 10^{-3}$	$7.9 \times 10^{-3}$	$4.7 \times 10^{-2}$	0.243	0.464	0.464	0.464	
1	0.25	100	0.25	$5.8 \times 10^{-7}$	$5.8 \times 10^{-6}$	$1.7 \times 10^{-5}$	$1.7 \times 10^{-4}$	$3.4 \times 10^{-4}$	$2.1 \times 10^{-3}$	$1.2 \times 10^{-2}$	0.080	0.0971	0.0971	
0.5	0.125	100	0.25	$1.4 \times 10^{-7}$	$1.4 \times 10^{-6}$	$4.3 \times 10^{-6}$	$4.3 \times 10^{-5}$	$8.6 \times 10^{-5}$	$5.2 \times 10^{-4}$	$3.1 \times 10^{-3}$	0.026	0.0485	0.0485	
0.1	0.025	100	0.25	$5.8 \times 10^{-9}$	$5.8 \times 10^{-8}$	$1.7 \times 10^{-7}$	$1.7 \times 10^{-6}$	$3.4 \times 10^{-6}$	$2.1 \times 10^{-5}$	$1.2 \times 10^{-4}$	$1.2 \times 10^{-3}$	$9.7 \times 10^{-3}$	$9.7 \times 10^{-3}$	
0.05	0.0125	100	0.25	$1.4 \times 10^{-9}$	$1.4 \times 10^{-8}$	$4.3 \times 10^{-8}$	$4.3 \times 10^{-7}$	$8.6 \times 10^{-7}$	$5.2 \times 10^{-6}$	$3.1 \times 10^{-5}$	$3.1 \times 10^{-4}$	$4.9 \times 10^{-3}$	$4.9 \times 10^{-3}$	
500	50	50	0.10	0.0287	0.286	0.854	7.89	13.7	21.7	21.7	21.7	21.7	21.7	
100	15	50	0.15	$1.7 \times 10^{-3}$	$1.7 \times 10^{-2}$	0.0514	0.509	1.00	4.28	5.41	5.41	5.41	5.41	
50	9	50	0.18	$5.2 \times 10^{-4}$	$5.2 \times 10^{-3}$	$1.5 \times 10^{-2}$	0.154	0.305	1.59	2.98	2.99	2.99	2.99	
10	2	50	0.20	$2.3 \times 10^{-5}$	$2.3 \times 10^{-4}$	$6.9 \times 10^{-4}$	$6.9 \times 10^{-3}$	0.0137	0.0810	0.400	0.632	0.632	0.632	
5	1.15	50	0.23	$6.6 \times 10^{-6}$	$6.6 \times 10^{-5}$	$2.0 \times 10^{-4}$	$2.0 \times 10^{-3}$	0.0039	0.0235	0.131	0.340	0.341	0.341	
1	0.25	50	0.25	$2.9 \times 10^{-7}$	$2.9 \times 10^{-6}$	$8.6 \times 10^{-6}$	$8.6 \times 10^{-5}$	$1.7 \times 10^{-4}$	0.00103	0.0061	0.0484	0.0712	0.0712	
0.5	0.125	50	0.25	$7.2 \times 10^{-8}$	$7.2 \times 10^{-7}$	$2.2 \times 10^{-6}$	$2.1 \times 10^{-5}$	$4.3 \times 10^{-5}$	$2.6 \times 10^{-4}$	0.00154	0.0142	0.0356	0.0356	
0.1	0.025	50	0.25	$2.9 \times 10^{-9}$	$2.9 \times 10^{-8}$	$8.6 \times 10^{-8}$	$8.6 \times 10^{-7}$	$1.7 \times 10^{-6}$	$1.0 \times 10^{-5}$	$6.2 \times 10^{-5}$	$6.1 \times 10^{-4}$	$7.1 \times 10^{-3}$	$7.1 \times 10^{-3}$	
0.05	0.0125	50	0.25	$7.2 \times 10^{-10}$	$7.2 \times 10^{-9}$	$2.2 \times 10^{-8}$	$2.2 \times 10^{-7}$	$4.3 \times 10^{-7}$	$2.6 \times 10^{-6}$	$1.5 \times 10^{-5}$	$1.5 \times 10^{-4}$	$3.6 \times 10^{-3}$	$3.6 \times 10^{-3}$	

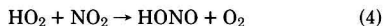
<sup>a</sup> The unit ppm used here is defined as [pressure (torr)/760] × 10<sup>6</sup>.



tion 1 and  $E_2 \approx 10 \text{ kcal mol}^{-1}$ . These data give further credence to the alternative Reaction 11 which, as we have seen, supports this choice of activation energies indirectly.

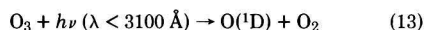
**Significance of Nitrous Acid Formation and Decay Reactions in Polluted Atmosphere.** The rate data found for Reactions 1 and 2 provide a new basis for the evaluation of the significance of these reactions in the atmosphere. They have been used to estimate the time dependence of the HONO pressure for various levels of  $\text{NO}_2$ , NO, and  $\text{H}_2\text{O}$  which are typical of those encountered near pollution sources and in ambient air. The results of these calculations are shown in Table III. Note that for very high  $\text{NO}_x$  levels which correspond to those encountered near power plant stacks and automotive exhaust pipes, the rate of HONO generation is very significant. For example, after only 30 s of elapsed time, the  $P_{\text{HONO}}$  has achieved the 1.7 ppm level for the high  $\text{NO}_x$  case. Obviously, dilution of the reactants occurs as the exhaust gases mix turbulently with the air, and no attempt has been made here to simulate that process. Observe from the results of Table III that the generation of nitrous acid slows significantly as the  $\text{NO}_x$ - $\text{H}_2\text{O}$  mixture reaches ambient levels of these pollutants. Although after only 10 min of contact between reactants in a mixture of  $\text{NO}_x$ - $\text{H}_2\text{O}$  of composition equivalent to that of power plant stack emissions, the  $P_{\text{HONO}}$  has reached 79% of its equilibrium value, the  $\text{NO}_x$ - $\text{H}_2\text{O}$  mixture at ambient levels has reached only 6% of its equilibrium levels of HONO after 60 h. We may conclude from the present data that HONO may be generated at a significant rate during the early stages of dilution of  $\text{NO}_x$ -rich exhaust gases. We must also conclude that Reactions 1 and 2 are unimportant in forming or removing HONO when ambient levels of  $\text{NO}_x$  are present.

It is believed that the oxidation of about 25% of the original NO to  $\text{NO}_2$  occurs in auto exhaust gases during the dilution process by Reaction 12, the near equivalent to Reaction 1, as we have seen. Thus, the significant occurrence of Reaction 1 as power plant and automotive exhaust gases mix with air should not be surprising. Present data suggest that HONO vapor will be generated especially efficiently in the evening and the early morning peak traffic hours as the rate of injection of  $\text{NO}_x$ -rich exhaust gases is high. It is reasonable that HONO pressures in the early morning hours may be a significant fraction of the HONO equilibrium pressures expected from the NO,  $\text{NO}_2$ , and  $\text{H}_2\text{O}$  ambient pressures present at this time. Thus, it appears likely that the photolysis of HONO can provide a reasonable boost to the primary generation rate of the HO-radical reactant which in consort with CO and hydrocarbons drives the NO to  $\text{NO}_2$  and generates the products of photochemical smog. Once this initial burst of HO-production has begun, the generation of HONO through the chain transfer Reaction 4 will likely be the major source of this species and will maintain a significant level of HONO as the smog development occurs.



In previous computer simulations of the chemistry of the  $\text{NO}_x$ -hydrocarbon-polluted atmospheres in which low ambient levels were assumed for the impurities, it has been recognized that the time dependence of the concentration of ozone and other products of photochemical smog is relatively insensitive to the choice of values for the rate constants  $k_1$  and  $k_2$ . This result was found even though  $k_1$  and  $k_2$  were varied from values near zero to the very high early estimates of Wayne and Yost (1, 3). Obviously, the acceptance of the present values for  $k_1$  and  $k_2$  leads to no significant alteration of previous mechanism considerations in

smog-forming reactions occurring at ambient pollutant concentrations. However, their use should lead to a boost in initial HO-generation rates in simulations of sunlight-irradiated,  $\text{NO}_x$ -polluted atmospheres and a shortening of the induction period for  $\text{NO} \rightarrow \text{NO}_2$  conversion and smog generation. However, the most significant result of these findings appears to relate to the chemistry which occurs in stack gas plumes. Those atmospheric scientists concerned with the chemistry within plumes should include Reactions 1-3 in their considerations and simulations. These appear to be important steps in the triggering of the chemical changes which occur, and, in our opinion, they provide a more significant rate of HO-radical generation in power plant plumes than the sunlight photolysis of ozone:



Ozone levels must remain quite low in the plume until a considerable fraction of the NO is converted to  $\text{NO}_2$ ;  $[\text{O}_3] \approx 0.02 [\text{NO}_2]/[\text{NO}]$  ppm for a solar zenith angle of  $40^\circ$ . Even at  $[\text{NO}_2]/[\text{NO}]$  ratios near unity, the rates of  $\text{O}(^1\text{D})$  and HO-radical formation from the sequence 13 and 14 will be much lower than the HO-radical formation rate from the HONO photolysis.

Although a significant effort has been made to minimize the heterogeneous reaction pathways in our present study of the Reactions 1 and 2, it is impossible to evaluate unambiguously the possible contribution of heterogeneous pathways to the measured reaction rates. However we recommend that the present estimates of  $k_1$  and  $k_2$  be adopted in atmospheric modeling studies, although it must be recognized that these are, at best, estimates of the upper limits to the true homogeneous rate constants.

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# Multielement and Chlorinated Hydrocarbon Analysis of Municipal Sewage Sludges of American Cities

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■ An analytical survey of 68 elements, dieldrin, and polychlorinated biphenyls (PCB's) was conducted in municipal sewage sludges sampled during 1972-73 from 16 American cities using several instrumental methods. Unusually elevated concentrations of certain toxic elements were found in sludges

from specific cities. Relatively high levels of gold and mercury in sludge from San Francisco possibly derived from geochemical sources. Fluorine was high in several cities which fluoridate their water. PCB's were highest in sludge from Schenectady.

Municipal sewage sludges result from the treatment of city sewage wastes containing human excreta, residues from food, and sometimes lumber processing, and a galaxy of industrial chemicals. These latter chemicals may derive from the manufacture of paper, textiles, rubber, plastics, leather, paints, detergents, drugs, agricultural chemicals and electrical

equipment, processes such as printing, engraving and petroleum refining, operation of blast furnaces, foundries, smelters, plating processes and laundries, and a host of other human activities. Upward of 100 million tons of this material are produced annually in this country. Disposal of it has included ocean dumping, burning, disposal in landfills, and limited use on lawns, ornamentals, forests, and agricultural land. Since these latter methods may cause environmental pollution, other approaches have included studies of its possible conversion to fuels such as methane or oil or as a soil conditioner and fertilizer in horticulture and agriculture. In addition to its content of industrial organics, chlorinated insecticides and pathogens (1), toxic elements in it confound its safe use as a soil amendment for plant growth.

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**Table I. Data Pertinent to Municipal Sludges Studied**

City	Sewage plant	Wastewater treatment scheme	Sludge handling scheme	Chemicals added	Ultimate sludge disposal method
Atlanta, Ga.	Intranchment Creek	Trickling filter	Digestion, drying beds		Landfill, fertilizer-soil conditioner
Cayuga Heights, N.Y.	Cayuga Heights	Sedimentation	Digestion	Lime	Land disposal
Chicago, Ill.	Several	Activated sludge	Aerobic and anaerobic digestion, heat drying		"Vertigreen" fertilizer-soil conditioner
Denver, Colo.	Metropolitan Denver, District #1	Activated sludge	Aerobic and anaerobic digestion, concentration and filtration	Ferric chloride, lime	Land disposal
Houston, Tex.	Southwest and Northside	Activated sludge	Aerobic and anaerobic digestion, dehydration		"Hou-actinite" fertilizer-soil conditioner
Ithaca, N.Y.	Ithaca	Trickling filter	Digestion, vacuum filtration	Ferric chloride, lime	Landfill, soil conditioner
Los Angeles, Calif.	Joint Water Pollution Control	Sedimentation	Digestion, centrifugation, drying beds	None	Fertilizer-soil conditioner
Miami, Fla.	Virginia Key	Aeration, sedimentation	Concentration, digestion, shallow lagoons	None	Fertilizer-soil conditioner
Milwaukee, Wis.	Several	Activated sludge	Aerobic and anaerobic digestion, heat drying		"Milorganite" fertilizer-soil conditioner
New York, N.Y.	Newtown Creek	Activated sludge	Thickening tanks, digestion	None	Ocean disposal
Philadelphia, Pa.	Northeast	Activated sludge	Digestion lagooning	None	Ocean disposal
San Francisco, Calif.	Richmond-Sunset	Sedimentation	Thickening tanks, digestion, elutriation, vacuum filtration	Ferric chloride	Parks, gardens
Schenectady, N.Y.	Anthony Street	Sedimentation	Digestion, vacuum filtration, heat drying	Ferric chloride, lime	"Orgro" fertilizer-soil conditioner
Seattle, Wash.	West Point	Sedimentation	Digestion, vacuum filtration or centrifuging		Landfill or soil conditioner
Syracuse, N.Y.	Metropolitan	Sedimentation, Activated sludge	Digestion	None	Pumped to Solvay Process waste beds
Washington, D.C.	Blue Plains	Sedimentation	Digestion	None	Land disposal

Table II. Concentrations of Elements and Chlorinated Hydrocarbons Found in Various Municipal Sludges

Constituent	Analytical method used	Atlanta	Cayuga Hgts.	Chicago	Denver	Houston	Ithaca	Los Angeles	Miami	Milwaukee	New York	Philadelphia	San Francisco	Schenectady	Seattle	Syracuse	Washington, D.C.	Cow manure
Parts per million (dry weight) in sludge from:																		
Dieldrin	EC <sup>a</sup>	0.26	<0.03	0.24	0.16	0.28	0.06	0.44	0.43	0.05	...	2.2	0.06	0.04	0.10	0.05	...	<0.01
PCB <sup>b</sup>	EC	3.80	0.79	11.60	1.60	0.35	4.30	4.00	8.50	2.20	...	4.80	<0.01	23.10	0.50	6.60	...	<0.01
As	S <sup>c</sup>	3.6	3.0	29	14	20.4	4.8	26.0	10.0	3.3	8.0	16.2	6.4	21.9	30.0	26.0	6.6	4.0
Au	NA <sup>d</sup>	0.90	1.00	0.77	0.25	1.04	0.50	0.99	5.65	0.21	1.46	0.48	7.00	2.00	1.10	0.34	0.76	0.0002
B	S	22	30	44	30	36	40	90	33	50	44	22	33	33	40	32	16.0	23.5
Ba	NA	595	272	623	632	485	1004	1066	938	344	417	533	542	828	504	322	892	268
Be	ES <sup>e</sup>	<15	<7	<6	<10	<4	<7	<11	<5	<4	<12	<7	<5	<13	<7	<13	...	0.10
Bi	SSMS <sup>f</sup>	13.3	8.7	55.8	17.4	49.0	15.2	10.8	31.0	14.0	7.6	10.2	4.5	0.03	8.2	6.6	...	16.0
Br	NA	37.1	13.7	41.3	15.3	30.2	20.0	53.2	165	16.4	123	35.9	48.2	33.2	44.1	24.8	27.3	31.0
Cd	ASV <sup>g</sup>	104.2	6.8	14.8	46.1	111.8	66.7	171.4	149.6	443.7	29.7	192.4	8.5	22.4	64.0	20.0	...	55.0
Ce	NA	92.8	12.4	34.9	43.9	26.3	18.6	27.2	63.1	26.2	70.7	30.5	14.2	15.8	37.0	48.6	94.0	55.0
Co	NA	9.4	3.9	3.7	8.8	6.3	10.5	16.8	17.6	4.3	6.2	15.6	5.3	15.6	9.4	5.1	15.1	5.9
Cr	FAA <sup>h</sup>	1320	169	207	936	3480	640	4925	1430	14000	646	2320	1500	458	1320	1000	1260	56
Cs	NA	1.40	1.00	0.91	1.23	0.76	0.98	0.99	0.56	0.45	0.85	1.60	0.99	0.66	0.90	1.01	2.9	1.48
Cu	FAA	1463	821	578	1370	1560	1300	2890	1200	1288	1890	2680	900	900	1170	1060	458	62
Dy	SSMS	4.3	1.5	3.5	0.8	2.6	19.8	17.0	0.6	7.2	1.7	1.2	3.9	0.7	1.3	4.2	...	1.0
Er	SSMS	1.3	0.4	0.2	1.2	0.6	2.3	4.5	0.7	2.0	0.5	0.6	0.9	0.4	0.4	1.4	...	0.7
Eu	SSMS	4.4	0.7	2.5	2.4	9.4	0.8	9.9	1.9	12.2	2.0	0.7	3.7	0.8	1.0	3.4	...	0.7
F	SSMS	370.5	314.9	297.6	48.0	13.8	88.2	198.8	86.4	49.5	5.1	281.2	738.7	5.2	2.2	9.1	...	6.6
Ga	SSMS	17.1	8.7	9.2	8.9	24.1	51.7	54.0	0.9	27.9	12.3	12.4	3.3	5.7	10.2	6.6	...	16.5
Gd	SSMS	7.0	1.1	3.4	2.7	4.5	19.8	22.7	2.8	17.5	6.5	1.5	4.1	1.8	2.5	4.0	...	1.5
Ge	SSMS	1.3	2.0	1.6	10.5	4.2	6.2	6.4	2.6	5.4	4.3	1.5	1.5	1.1	1.7	3.6	...	19.1
Hf	NA	3.0	1.6	2.2	3.7	2.0	10.7	2.7	1.0	1.8	1.5	2.9	1.3	7.0	3.7	3.3	4.6	4.9
Hg	FL <sup>i</sup>	6.9	10.8	6.1	3.6	3.8	13.6	7.1	15.5	3.4	15.0	4.7	18.0	9.1	8.2	6.4	5.8	0.2
Ho	SSMS	0.48	0.13	0.07	0.41	0.21	0.46	0.51	0.67	0.38	0.53	0.18	0.28	0.14	0.09	0.31	...	0.36
I	NA	3.1	8.2	14.8	14.3	7.6	7.4	17.1	7.7	10.3	11.8	10.8	3.6	1.0	2.0	4.0	...	4.6
In	NA	0.08	0.23	0.10	0.18	3.7	0.26	0.17	1.30	0.07	0.16	0.58	0.08	0.12	0.20	0.48	0.50	1.40
Ir	SSMS	0.10	0.21	0.03	0.13	0.10	0.46	0.16	0.26	0.20	0.05	0.07	0.18	0.04	0.05	0.20	...	0.14
La	NA	29.6	6.4	11.5	9.3	10.9	11.9	380	7.1	33.9	14.1	13.4	5.1	7.6	9.7	12.8	7.9	23.7
Lu	NA	0.25	0.06	0.09	0.06	0.08	0.15	0.09	0.04	0.04	0.24	0.14	0.08	0.11	0.14	0.12	0.34	0.60
Mn	NA	267	128	95	224	102	527	116	32	134	152	95	113	235	350	216	323	286
Mo	NA	6.0	1.2	10.8	18.1	9.8	21	40	37	32.9	5.0	8.1	2.2	25.5	2.3	4.5	3.6	13.9
Nd	SSMS	2.0	1.1	3.4	2.6	2.2	3.2	3.3	1.4	8.6	1.1	1.5	2.0	0.6	0.6	3.8	...	2.5
Ni	FAA	169	36.4	51.2	562	102	166	402	453	360	140	432	223	72	153	211	...	29
Os	SSMS	0.29	0.19	0.07	0.20	3.18	1.35	0.47	0.15	0.59	0.08	0.09	0.17	0.06	0.06	0.22	...	0.10
Pb	ASV	1445	136	605	1011	2236	329	3065	1467	2253	1976	7627	2521	598	2411	1412	498	16.2
Pd	SSMS	5.2	0.5	11.7	5.6	11.2	5.2	13.5	2.6	16.2	1.1	1.4	3.9	0.32	0.9	2.1	...	3.8
Pr	SSMS	3.7	4.9	3.1	3.3	2.7	3.5	11.9	5.3	15.8	4.2	0.8	3.9	1.6	1.1	7.1	...	10.7
Pt	SSMS	0.10	0.23	0.07	0.25	0.20	0.64	0.44	0.12	0.38	0.11	0.74	0.18	0.08	0.05	0.18	...	0.14
Re	NA	46.2	28.7	31.1	46.4	18.3	25.7	19.3	4.5	4.3	32.7	30.9	25.1	43.0	24.3	46.1	94.6	88.9
Rb	SSMS	0.05	0.12	0.03	0.12	0.09	0.21	0.98	0.07	0.19	0.05	0.04	0.09	0.04	0.03	0.10	...	0.06
Ru	SSMS	0.58	0.52	0.21	1.31	7.05	3.19	0.87	0.94	0.27	0.30	1.01	2.08	0.22	0.27	0.51	...	0.38
Sb	NA	14.6	2.6	4.4	3.5	9.9	5.9	14.3	14.8	4.2	10.6	44.4	5.2	9.1	10.8	5.4	10.6	0.5
Sc	NA	7.1	1.5	2.0	1.6	1.2	1.7	1.1	0.5	0.8	3.1	2.8	2.2	2.1	5.2	2.1	5.7	5.2
Se	F <sup>j</sup>	1.7	1.7	1.7	3.5	...	4.6	8.7	2.9	1.7	2.7	3.4	3.0	4.7	2.7	2.1	1.9	2.4

Element	5.0	1.0	3.1	2.0	2.2	1.4	14.2	1.4	1.5	6.7	2.6	1.1	1.5	2.0	2.0	8.3	5.2
Na	146	128	166	161	234	111	209	269	133	202	189	133	189	373	191	8.3	3.6
Sn	42	68	259	262	138	67	360	259	94	334	322	176	224	186	210	291	81
Ta	0.53	0.18	0.20	0.35	0.36	0.43	1.2	0.33	0.11	0.49	0.66	0.31	1.45	0.41	0.92	0.58	0.38
Tb	0.89	0.40	0.73	1.20	0.49	4.26	4.83	2.23	3.65	0.50	0.34	0.91	0.38	0.27	0.44	...	0.29
Te	SSMS	0.09	0.22	0.11	0.45	1.52	0.54	0.12	0.36	0.10	0.25	0.05	0.07	0.21	0.17	...	0.22
Th	NA	12.8	3.1	5.6	4.6	11.1	7.0	2.3	2.6	7.8	6.5	3.5	4.4	3.9	5.6	16.3	...
Ti	NA	4580	1080	1340	1680	2160	3170	2360	1580	2050	2680	1910	1960	2560	1550	4260	2800
Tm	SSMS	0.49	0.13	0.07	0.65	0.11	0.78	0.78	3.31	0.68	0.37	1.0	0.08	0.06	0.32	...	0.14
U	NA	0.8	1.2	6.4	2.9	4.8	3.4	3.7	2.1	1.0	0.9	2.0	3.3	3.2	3.0	1.6	2.4
V	NA	50.4	18.8	48.7	34.1	26.6	14.8	35.7	34.8	22.9	38.4	35.4	36.7	57.3	50.1	91.5	43.2
W	NA	5.1	0.9	4.2	5.6	41.1	17.7	14.7	22.9	9.5	32.1	5.1	99.6	21.1	15.3	3.3	2.5
Y	SSMS	3.7	10.1	1.5	4.9	4.1	4.3	5.5	0.9	7.7	2.1	3.7	0.8	1.1	3.6	...	2.8
Yb	NA	1.30	0.40	0.61	0.33	0.36	0.42	0.57	0.17	0.29	0.64	0.62	0.61	0.52	0.40	1.6	1.78
Zn	NA	2838	560	1160	2860	2560	1700	4590	1400	1370	6890	601	1090	1830	1840	1475	71
Zr	SSMS	18.1	12.7	22.3	31.6	39.6	86.6	16.6	14.4	5.4	11.1	15.8	92.1	4.8	37.1	...	5.5
Al	NA	3.47	0.97	1.36	1.34	0.81	1.83	0.91	1.74	1.29	2.34	1.44	1.21	2.70	1.91	5.12	2.88
Ca	NA	2.70	11.64	2.53	1.55	0.77	5.45	4.01	4.28	0.86	1.99	1.07	7.93	2.64	6.55	2.40	26.4
Cl	NA	0.05	0.20	0.10	0.39	0.66	0.20	0.39	1.02	0.22	0.85	0.11	0.39	0.22	0.28	0.34	0.18
Fe	NA	2.42	1.74	0.88	8.28	3.23	5.74	2.07	0.95	4.30	1.99	3.05	3.46	2.71	1.44	4.50	1.59
K	NA	0.56	0.29	0.72	3.87	0.27	0.38	0.47	0.29	0.84	1.39	2.80	0.42	1.56	1.59	0.71	3.29
Mg	NA	1.13	0.50	0.54	0.33	0.20	0.32	0.57	0.75	0.50	0.60	0.81	0.81	0.82	0.67	0.55	0.73
N	NA	2.45	1.48	3.99	3.14	5.43	1.62	2.19	3.34	5.80	2.30	2.16	1.81	2.62	2.07	1.25	1.25
Na	NA	0.15	0.17	0.36	0.18	0.11	0.08	0.68	1.19	0.16	1.54	0.37	0.30	0.86	0.60	0.11	4.92
P	NA	1.40	0.96	1.62	1.32	1.60	2.72	0.68	1.66	1.84	1.92	1.16	1.20	1.80	1.40	...	0.90
Ash	57.3	57.7	49.5	37.8	31.5	58.9	43.2	39.7	30.9	46.7	53.2	41.4	59.4	56.7	51.8	...	63.5

<sup>a</sup> Electron capture gas chromatography. <sup>b</sup> Determined as Arcochlor. <sup>c</sup> Spectrophotometric. <sup>d</sup> Neutron activation. <sup>e</sup> Emission spectroscopy. <sup>f</sup> Spark source mass spectrometry. <sup>g</sup> Anodic stripping voltammetry. <sup>h</sup> Furnace atomic absorption. <sup>i</sup> Flameless atomic absorption. <sup>j</sup> Fluorescence. <sup>k</sup> Kjeldahl.

Municipal sludges may contain virtually any element depending on the spectrum of industries served, their changing rates of production, and periodic relocation. Analytical surveys of a few to several toxic elements in sludges have been conducted in England (2), Canada (3), and the United States (4-6). In the work reported, an analytical survey of 68 elements, dieldrin, and polychlorinated biphenyls (PCB's) was conducted of sewage sludges from various American cities.

### Experimental

In 1972 and 1973 a description of our proposed study was sent to 35 cities with a request that they participate and return a representative sample of their sludge to us for analysis. The cities which responded and the data they provided pertaining to their sludge treatment are listed in Table I. Cayuga Heights is a small village just north of Ithaca. Its sludge is almost entirely composed of domestic waste. The cow manure sample was obtained as a dehydrated bagged commercial product of Agway, Inc. It was considered pertinent to compare the element composition of cow manure as an accepted soil amendment with that of municipal sludges. The sludge samples were air-dried, mixed in a Lucite twin shell blender, and subsampled for analysis.

The determination of dieldrin and PCB's was performed by Soxhlet extraction, isolation using acetonitrile partitioning and column chromatography on Florisil (7). Final determination was made by electron affinity gas chromatography using a column 6 ft long containing 10% OV-17 on 80-100 mesh Gas Chrom Q operated at 220°C.

Analysis for elements by nondestructive neutron activation was carried out. Weighed samples were placed in 0.4-dram polyethylene vials (1.5 cm i.d. × 2 cm high). The samples were irradiated three times, once for a short period in a pure thermal flux to eliminate induced Si activity leading to <sup>28</sup>Al (which varied depending on Na and Cl content but on the order of 1 min) and again in a mixed fast and thermal flux for a comparably brief period, and finally for a period of approximately 8 h. The neutron fluxes to which the samples were exposed were respectively 4 × 10<sup>10</sup> n/m<sup>2</sup>-s, 1.2 × 10<sup>12</sup> n/cm<sup>2</sup>-s, and 1.3 × 10<sup>12</sup> n/cm<sup>2</sup>-s for the long irradiation. After the short irradiations, the samples were counted within a few minutes on a Ge(Li) counting system for a period of 8 min. Data were acquired using a Nuclear Data Model 4420 multichannel analyzer and stored on magnetic tape for later processing. For the long irradiations, the samples were first counted as soon as practical, considering the level of the activity due to sodium. This period of time varied from 2 to 5 days after the end of the irradiation. The samples were counted again after a period of 15-20 days. Each sample, therefore, was irradiated three times and counted four times.

The counts stored were in the form of gamma spectra containing peaks which could be attributed to the gamma emissions from the radioactive constituents in the samples. For some elements, only a single peak represents the element, whereas in other cases two or more isotopes with possibly several gammas could be employed for quantitative measurements. Repeated tests have demonstrated the capability of the computer program to accurately fit the peaks with a gaussian curve, or in some cases overlapping gaussian curves, situated on a background usually represented by a quadratic polynomial, although for very narrow peaks the background can be represented by a linear function. For quantitative measurements, peak areas are compared to results obtained with known standards, usually well-known chemical compounds or pure elements, but on other occasions to documented samples.

Recently, for example, well-known geologic materials and coal samples obtained from the Bureau of Standards have

been processed with agreement well within the accepted range of variability being found for nearly every element detected. To ascertain that continued quality be maintained, groups of three compounds of selected elements are periodically processed with the identity of the elements being changed each time. In the group of test elements processed, nearest to the experiments reported here (Na, Mg, Al, Ti, Cr, Mn, Cu, Mo, Cd, Sn, Ta, W, U, Zn, Se, and Sb), no net variance exceeding 5% compared to the previous standard values was found, and most were within 1–2%. However, in a few cases, individual compounds or specimens were unsuitable for use as standards.

Since the comparison library has been run under exactly comparable conditions, for all the elements, using the same reactor operated at the same power or flux levels and counted under the same geometric conditions at closely similar levels of activities, the quality of the data should be essentially limited only by the statistical variance introduced by the relative size of the peaks employed and the background on which the peaks are superimposed. However, in a few cases not enough data on possible interference peaks can be derived from the sample data and in such cases (e.g., for Ni), the interference potential is considered so great that no reliable values can be quoted.

Other methods of analysis which were employed required preliminary ashing of the samples. Up to 1 g of sample was dry ashed at 475 °C by the method of Gajan and Larry (8).

Spark source mass spectrometric analysis was performed using a subsample of the ash. The ash was thoroughly mixed with an equal weight of high-purity graphite (Ultra Carbon Corp., 1M-VSP outgassed ultra superior purity) by the usual method (9). The electrodes were sparked against each other under the following conditions: repetition rate: 100 pulses/s; pulse length: 100  $\mu$ s; source pressure:  $1 \times 10^{-7}$  torr while sparking with cryosorption pumping; ion accelerating voltage: 22 kV. Ilford Q-2 photoplates were used as an ion detector. Results were calculated and corrected by the method of Owens and Giardino (10). The lead content of the sludges (as determined by anodic stripping voltammetry) was used as an internal standard for the method.

Emission spectroscopy was performed using a Bausch and Lomb dual grating spectrograph with a Model RC-2 Baird atomic microphotometer. The standards consisted of high-purity (99.999%) oxides of Si, Al, Ca, Fe, and Mg spiked with 12.7, 25.4, 63.5, and 127  $\mu$ g/g of the 49 element Spex Mix (1.27% each element). Unspiked matrix served as a blank. The standards and the ashed samples were mixed 1:9 with UCP-2 graphite containing 0.01% GeO<sub>2</sub>. These were fired in duplicate using a DC arc. A Stallwood Jet with 70% argon and 30% oxygen atmosphere surrounded the crater electrode.

Cadmium and lead were determined by conventional stripping voltammetry using a Princeton Applied Research Corp. Model 174 polarographic analyzer (8). Chromium, copper, and nickel were determined by furnace atomic absorption using a Perkin Elmer Model 303 spectrophotometer equipped with an HGA-2000 furnace. Mercury was determined by flameless atomic absorption analysis following combustion of the dry sample using an oxygen flask (11).

The determination of selenium was accomplished by a modification of the method of Olsen (12) employing wet digestion of the sample and measurement of the fluorescence of piazselenol resulting from reaction of selenium with 2,3-diaminonaphthalene. Boron was determined by the curcumin spectrophotometric procedure (13). Arsenic was determined by distillation of arsine and determination using the silver diethyldithiocarbamate spectrophotometric procedure (14, 15). Phosphorus was determined by the molybdivanadophosphoric acid spectrophotometric method (13). Nitrogen was determined by the Kjeldahl method.

## Results and Discussion

The results of analysis of the sludge samples are listed in Table II. Except for potassium which appears elevated (above 2%) in several of the sludges, the range of concentrations of boron, cadmium, copper, chromium, lead, mercury, nickel, nitrogen, phosphorus, and zinc reported here agrees with those for these elements in typical municipal sludges (16).

Some interesting observations are also apparent. The relatively high level of PCB's in sludge from Schenectady may derive from the predominant manufacture of electrical equipment there. Gold is especially high in the Miami and San Francisco sludges. The San Francisco sludge was produced at the Richmond-Sunset Treatment Plant receiving mainly domestic wastes. The gold may in part originate from its presence as colloidal gold in the natural waters of the cities' watershed area. Notably, mercury is also high in these same two sludges. Mercury and gold are often found in association (17), and gold and mercury mining has abounded in the San Francisco area. Of course, mercury in sludge also results from its many industrial applications.

Several cities' sludges are also high in fluorine. As well as industrial contributions of the element, its presence in sludges could also derive from municipal fluoridation of water and elevated natural levels of the element in various geographical areas. Cities such as Chicago, Denver, Miami, Milwaukee, Philadelphia, and San Francisco fluoridate the water supply (18). The natural fluoride concentrations in city water supplies along the northeastern seaboard average from 0.02 to 0.1 ppm (19), whereas in midwestern, western, and southern states the average is above 0.2 ppm (20, 21).

A number of elements are notably high in sludges from specific cities. These include antimony (Philadelphia), barium (Ithaca and Los Angeles), cadmium and chromium (Milwaukee), copper and lead (Philadelphia), nickel (Denver, Los Angeles, Miami, Milwaukee, and Philadelphia), tin (Philadelphia), uranium (Chicago and Denver), zinc (Los Angeles and Philadelphia), and zirconium (Ithaca). The sources of some of the rarer elements such as cerium, gallium, germanium, hafnium, lanthanum, praseodymium, scandium, samarium, and others are speculative. Industrial uses are one source. Shacklette et al. (22) in an extensive national survey reported soils in the United States to contain the following concentrations of elements: gallium (<5–70), lanthanum (<30–200), and scandium (<5–50). Relatively high concentrations of rare earth elements have been reported in many plants (23–26). Complexation of rare earth ions by organic chelates in soils has been suggested as a mechanism leading to their availability to plants (27). A large number of rare earth elements were recently reported at surprisingly high concentrations in aquatic plants (28). Germanium found at a concentration of 19.1 ppm in the cow manure sample in this study has been reported to be absorbed from soils by cereal crops and to be rapidly excreted by animals (29).

When considering the application of municipal sludges to agricultural soils, availability of specific elements to edible plants must be considered. Of the elements which have been studied, arsenic, barium, chromium, fluorine, lead, and mercury tend to be excluded by plants. Boron, cadmium, cobalt, copper, manganese, molybdenum, nickel, selenium, zinc, and possibly antimony tend to be absorbed (30, 31). Many factors control ion uptake, however, such as soil type, pH, organic matter, redox potential, and plant species. It is also important to remember that municipal sludge from largely domestic sources may also be unsafe for agricultural uses since a major portion of copper, cadmium, chromium, nickel, and zinc in wastewater can derive from domestic uses (32).

In summary, interpretation of the data presented here would be obviated if specific municipal sludges could be



monitored periodically rather than just once. As pointed out in the introduction, municipal sludges are highly variable in composition with time and location of sampling for the reasons given. If we assume a sludge sample is representative, a broad-range multielement analysis can be quite revealing, and the data obtained are crucial in deciding what the ultimate means of safe and hopefully useful sludge disposal is to be.

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## Industrial Waste Disposal. Excess Sulfuric Acid Neutralization with Copper Smelter Slag

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■ An economic process for the disposal of two industrial waste products, sulfuric acid and copper reverberatory slag, has been developed. Metal values are effectively extracted from the slag, and acid is consumed in a nonpolluting way. The

process is a leach lime roast procedure that consumes 1 ton of acid per ton of slag while permitting extraction of 85% of the copper and zinc. Ninety percent of the sulfur is retained, and a solid storable product is produced.

Production of sulfuric acid is the most important method for removing sulfur oxides from copper, lead, and zinc smelter gases. The requirement to meet emission standards, which in some states is being established at 90% removal of input sulfur to the smelter, has necessitated expansions of the contact acid plants at many nonferrous sulfide smelters. It appears, therefore, that sulfuric acid production from smelters will be significant for some years. There are several new potential

processes under development and evaluation (1-4), but the present significant investment in acid plants under construction denotes a tremendous growth in sulfuric acid production from nonferrous smelters in the future (5).

Of the sulfur entering the smelters in 1960, 387 000 tons (20%) were removed as sulfuric acid; in 1970, 600 000 tons (26%) of sulfur from smelter feed were recovered as acid (5). If growth continues as expected and the 90% sulfur recovery criteria are met, 2 598 000 tons of sulfur as sulfuric acid, or other forms of by-product sulfur, are anticipated by 1980 from smelters alone. Furthermore, as more sulfur and its compounds are recovered in the future from coal and petroleum

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**Table I. Microprobe Analysis<sup>a</sup> of As Received Reverberatory Slags**

Slag source	Glass matrix, %				Matte globules, %			
	Cu	Zn	Fe	S	Cu	Zn	Fe	S
Smelter A	0.1-0.6	6.5-7.2	19-25	0.06-0.1	48-55	1.0-6.2	14-27	1.5-2.7
Smelter B	0.2 <sup>b</sup>		23	0.05	37-47	1.8-2.3	17-21	1.7
Smelter C	0.1-0.2	0.2-1.8	15-28	0.05-0.06	28-49	0.2-1.7	11-28	1.8-2.4

<sup>a</sup> Data source: A.R.L. Microprobe, Idaho Bureau of Mines, University of Idaho, Moscow, Idaho. <sup>b</sup> Single number values are the result of a single microprobe test. A range of values was not determined.

**Table II. Head Analysis on Smelter Slags Used in LLR Tests**

Smelter	Composition, %		
	Cu	Zn	Fe
A	0.65	2.69	32.84
B	0.35	2.08	31.46
C	0.74	0.34	34.91

**Table III. Screen Analysis of Pulverized Slag**

Mesh <sup>a</sup>	%	Mesh <sup>a</sup>	%
+48	1.7	-150, +200	10.6
-48, +65	5.1	-200, +270	9.1
-65, +100	15.6	-270, +325	6.3
-100, +150	18.7	-325	32.8

<sup>a</sup> Tyler Standard Series.

products, estimates indicate that by 1980 only 43% of the total sulfur produced will be needed to satisfy domestic needs (5). With respect to smelter-produced sulfuric acid, nearly all plants are located away from potential or actual markets. It appears likely that part of the sulfur products must be disposed of as solid wastes, such as gypsum (CaSO<sub>4</sub>), or converted to elemental sulfur.

Smelters that produce more acid than they can sell must dispose of the excess product in some environmentally acceptable manner. At present, it appears that most excess sulfuric acid will be neutralized with limestone or lime to yield gypsum. The estimated (7) cost of neutralizing acid is \$10/ton if limestone quarries are near the smelter; much more if limestone or lime must be shipped to the smelter sites.

An alternative to the limestone neutralization process is proposed, i.e., smelter slag, a readily available product, can be used as the neutralizing agent. In addition to acid neutralization, metal values contained within the slag can be recovered to offset the treatment costs.

The 16 United States smelters produced approximately 1.4 million tons of copper in 1969 from an estimated 6.3 million tons of concentrates and precipitates (8). The slag, as a throw-away product, amounted to about 4 million tons. Copper reverberatory slags contain 0.5-1% copper and 1.5-4.5% zinc (9). Therefore, the discarded slag contains 20 000-40 000 tons of unrecovered copper and 60 000-180 000 tons of unrecovered zinc.

There are an estimated 200 million tons of slag reserves in the United States. These reserves could also be treated for metal value recovery. This would require producing greater tonnages of acid than are available at smelter sites. Elemental sulfur recovered from coal and petroleum processing could be economically shipped to smelter sites for conversion into sulfuric acid.

## Experimental

The slag samples used in this study were all water quenched, physically granulated, irregularly shaped, and fractured particles. Each slag particle is actually an amorphous siliceous matrix containing a random distribution of discrete mineral particles, matte globules, and metal globules. Although the constitution of copper reverberatory slag varies, it can be roughly classified as silicates, sulfides, oxides, and free metals (10-14).

The distribution of copper, iron, and zinc in the phases noted above for three smelter slags was determined by electron microprobe analysis (Table I). The metal contents for the samples investigated in this study are presented in Table II.

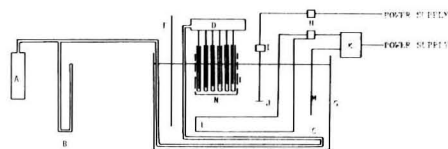
The experimental procedure for the leach lime roast (LLR) process is conveniently divided into three stages, quick leach, lime roast, and final leach.

**Quick Leach.** As received, reverberatory slags were ground through a BECO pulverizer. The particle size distribution of the pulverized sample is given in Table III.

Pulverized slag is readily attacked by sulfuric acid. However, the temperature, acid concentration, and time of reaction must be carefully controlled to prevent the formation of silica gel. The formation of silica gel prevents effective liquid-solid separation (15-18). A leaching technique was developed by Lindblad and Dufresne (19) that is extremely rapid and eliminates the silica gel problem. Therefore, their leaching technique (quick leach) was adopted and used for the initial preparation stage.

The quick leach procedure makes use of the heat of dilution to accelerate reaction rates. One part by weight of pulverized slag is slurred with one part concentrated sulfuric acid. To this is added one part distilled water. A vigorous reaction is promoted, the temperature rises, water is driven off as steam, and the reaction is essentially complete in 1-5 min. A semidry powder that is primarily a mixture of hydrated iron sulfates results. The glassy matrix is destroyed, and the entrapped globules of matte and concentrate particles are released for further treatment.

**Lime Roast.** The purpose of the roast stage is to promote the formation of copper and zinc sulfates and to oxidize a

**Figure 1. Leaching apparatus (oxygen gas agitation)**

- A. Oxygen gas tank
- B. Manometer
- C. Copper coil
- D. Gas distributor
- E. Test tube battery & holder
- F. Thermometer
- G. Thermostated water bath
- H. Powerstat
- I. Driving motor
- J. Auxiliary stirrer
- K. Temperature controller
- L. Heating element
- M. Thermostat
- N. Leaching solution

portion of the iron. During roasting, iron sulfate is oxidized with the release of sulfur dioxide. Lime in the roast mixture acts as an in-situ getter for the sulfur dioxide. The concept is similar to that of Barlett and Haung (20) and the U.S. Bureau of Mines (21) for treating copper concentrates. Sulfur is consumed in a nonpolluting way and produces gypsum. Iron is oxidized during the roast and is therefore not soluble in the final leach. Copper and zinc are sulfated during the roast and can be effectively extracted by an acid or water leach.

After the quick leach residue was completely dry, lime was added. This mixed slag product was shaped into small spherical pellets about half an inch in diameter. Some distilled water was necessary to form the pellets. These wet pellets were dried overnight at about 35 °C in a laboratory oven. After the pellets were completely dry, they were placed in a fireclay roasting dish and charged into a preheated furnace. At the end of the roast, the sample dish was removed from the furnace and allowed to cool in the air.

Most of the pellets were completely dry before roasting. However, tests were also performed with wet pellets prepared as above but not oven-dried. Partially dried pellets were also tested. The final extraction results showed little difference. Therefore, the degree of dryness of the pellets before roasting is not considered a variable of importance.

Sulfur balances were conducted to determine sulfur retention as a function of several variables, e.g., roast time, roast temperature, lime content.

**Final Leach.** After cooling, the roasted pellets were ground to a fine powder and leached. For the sake of comparison, every roasted sample was leached in both 30 °C, 4.8 N sulfuric acid for 30 min and 80 °C hot water for 15 min. Due to the large numbers of samples, an easy and rapid leaching system

was developed. The apparatus for this rapid test is illustrated in Figure 1.

This device consisted of a battery of six test tubes held in a thermostated water bath capable of temperature control to  $\pm 1$  °C. Six different samples could be leached at the same time. Each sample was agitated by oxygen. The agitation gas passed through a mercury manometer which provided control of the gas pressure to 1 mm. The gas was preheated to the water bath temperature during passage through a copper coil immersed in the water bath. The leach solution was thus agitated by the compressed oxygen gas at the desired leach temperature. The preheated gas was introduced into the reaction tubes through a gas distributor. The attached glass distribution tubes were of uniform shape and outlet diameter.

The battery of test tubes, each containing 30 cc of leach solution, was brought to the leach temperature by the thermostated water bath. Approximately 1 g of ground sample was added to each test tube, and time was recorded for each sample. Agitation was adjusted sufficient to keep all the samples in suspension. At the end of each leach period, the slurry was filtered immediately. The leach solution was diluted to 100 cc. Subsequent dilution was necessary in some cases, depending on the dissolved metal content. Metal content was determined by atomic adsorption spectrophotometry. Before leaching, part of the ground roasted sample was taken for the purpose of head analysis. The head sample was digested in hydrofluoric acid and concentrated nitric acid and diluted to the proper concentration, and metal contents were determined by atomic adsorption spectrophotometric analysis. With analyses before and after leaching, the percent metal extraction by the leach solution was obtained. The analytical work for determination of copper, zinc, and iron concentrations was performed at the Montana Tech Foundation Mineral Research Center, Butte Industrial Park, Butte, Mont., with a Perkin-Elmer Model 403 atomic adsorption spectrophotometer.

### Summary of Experimental Results

The quick leach product was mixed with lime, shaped into spherical pellets, and roasted. A series of test roasts was run to determine optimum conditions of initial slag particle size, roasting time, and roasting temperature. The roasted products from these tests were leached under two solution conditions as described previously. Further leach tests investigating solution normality, solution temperature, leach time, pulp density, and agitation rate were conducted on roasted products treated by optimum laboratory roast conditions.

Example data plots depicting influence of roast time and roast temperature on metal extraction are given in Figure 2. (The data presented on the figures are in most instances an average of at least two tests, sometimes as many as six tests, performed under similar experimental conditions. The reproducibility for a given set of test conditions, in most cases, fell within a range of 10%. If we consider the heterogeneous nature of the starting slag, the range of 10% is considered acceptable to delineate trends.) A roast temperature of 600 °C appears optimum for acceptable copper and zinc extraction and low iron extraction.

The parameter found to have the greatest influence on copper and zinc extraction was lime content. As shown in Figure 3, the presence of lime depresses both copper and zinc extraction. However, this depression in extraction is acceptable for 6 wt % lime. Some lime is necessary to accomplish 90% retention of the sulfur (Figure 4, Table IV) in the solid product residue, i.e., at 600 °C, 1/2 h roast, 6% lime is sufficient to retain 90% of the sulfur in the solids and yet allows 80–85% extraction of the copper and zinc in either an acid or water leach.

Leach parameters were investigated following the opti-

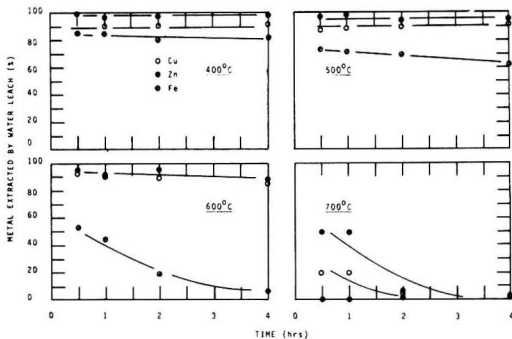


Figure 2. Influence of roasting time on metal extraction: 0% lime, water leach

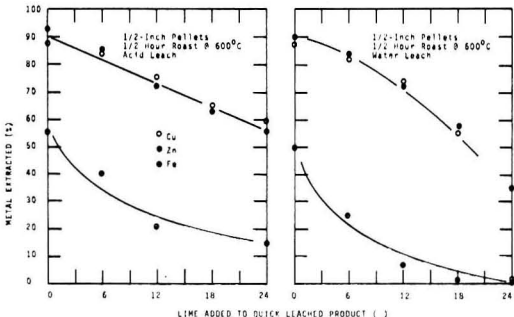


Figure 3. Influence of lime content on metal extraction from roasted products

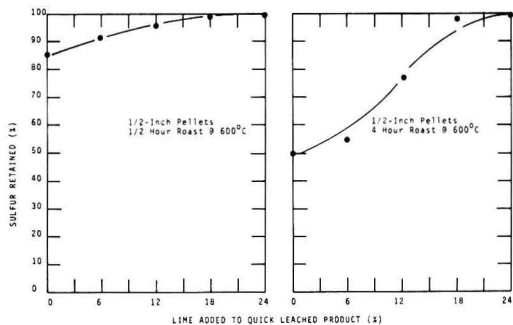


Figure 4. Influence of lime content on sulfur retention

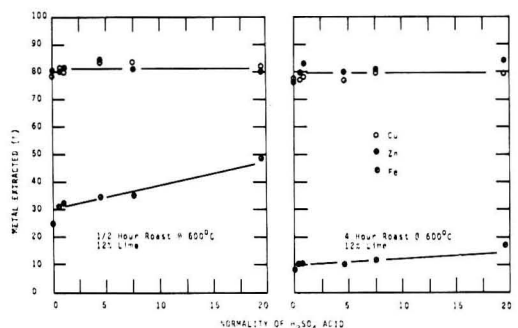


Figure 5. Influence of normality on metal extraction from roasted products

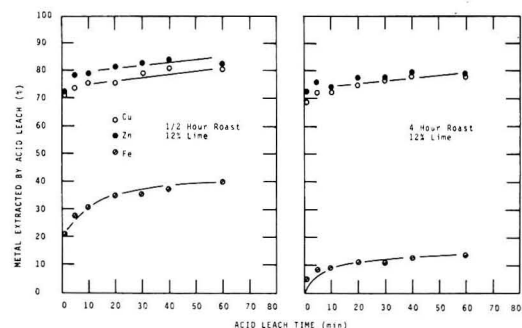


Figure 6. Influence of acid leach time on metal extraction from 600 °C roasted products

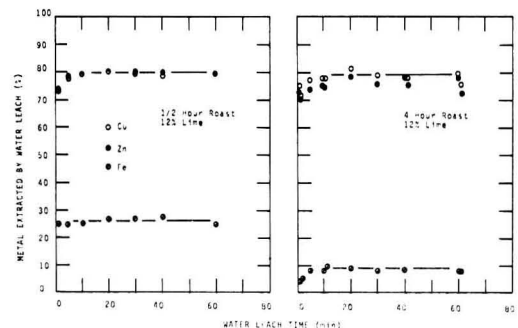


Figure 7. Influence of water leach time on metal extraction from 600 °C roasted products

Table IV. Influence of Lime Content<sup>a</sup> on Sulfur Retention During 600 °C Roast

Lime content, %	Sulfur retained, %	
	1/2-h roast	4-h roast
0	83.7, 84.6, 90.0	47.9, 50.2, 53.5
6	89.8, 95.3	53.3, 56.4
12	88.4, 91.8, 93.0, 94.9, 100.0	69.3, 77.7, 80.1
18	99.0, 100.0	97.4, 99.3
24	98.5, 100.0, 100.0	100.0, 100.0, 100.0

<sup>a</sup> Percent lime added to quick leached product.

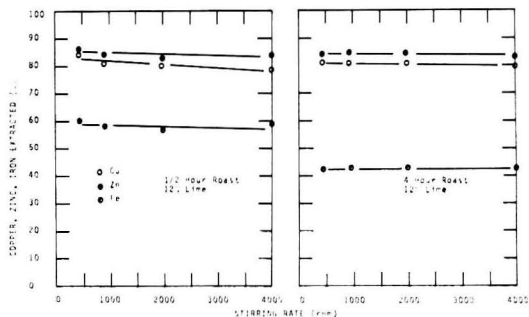


Figure 8. Influence of agitation rate on metal extraction from roasted products: acid leach

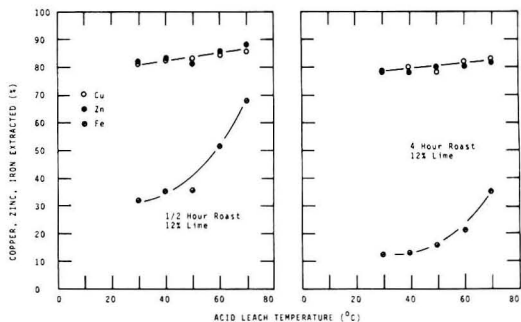


Figure 9. Influence of acid leach temperature on metal extraction from roasted products

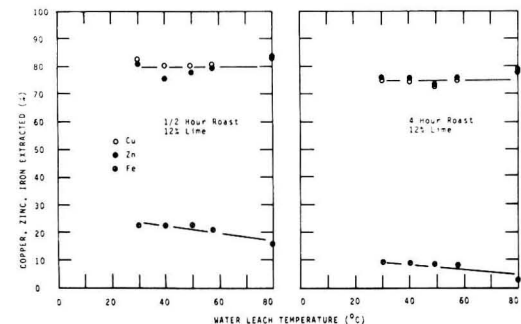


Figure 10. Influence of water leach temperature on metal extraction from roasted products

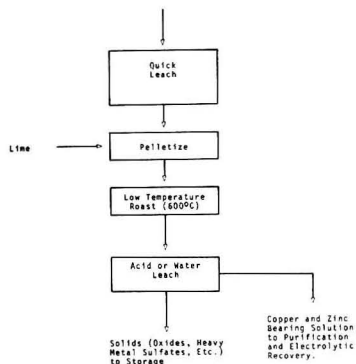


Figure 11. Leach lime roast process sequence

zation of roast parameters. The parameters found to have little influence on final copper and zinc extraction from products roasted at 600 °C for ½ h were: acid normality, Figure 5; leaching time, Figures 6, 7; agitation rate, Figure 8; and leach solution temperature, Figures 9, 10.

A proposed treatment resulting from the present laboratory study is shown in Figure 11. A comparison of the response of various smelter slags to leaching is shown in Figure 12.

### Conclusions

The leach lime roast procedure appears to have good possibilities for commercial application. Seventy-five to 85% copper and zinc but less than 30% iron are extracted by a simple water or dilute acid leach after a simple pelletization (6% lime) and low-temperature (600 °C) air roast (½ h).

As shown in Figure 12, some slags respond more effectively to the treatment procedure than others. Each individual smelter slag should therefore be studied for its response to selected experimental parameters.

The inclusion of lime in the mixture to be roasted allows 90% of the sulfur to be retained in the solids. This can be disposed of very easily. Air pollution is apparently not a problem, and the disposal of iron sulfate bearing solutions is minimized.

A very desirable feature in a commercial process sequence is to have flexibility in parameter control. This appears to be true in the LLR process, i.e.:

A convenient roast time of ½ h is sufficient. However, interpolating the data suggests times to 1 h would not seriously affect copper and zinc extractions.

Roast temperature should be held near 600 °C but certainly a ±25° range could be tolerated.

Pellet size has very little influence.

Lime content should be controlled at 6 ± 2.5%.

The leach solution conditions for treating the roasted products appear to have rather wide ranges of applicability: leach time: 10 min to 1 h; leach solution normality: water to concentrated acids; solution temperature: water leach extractions are independent of temperature and copper and zinc extractions are independent of acid temperature up to 70 °C, but the solution temperature should be kept low to minimize iron extraction; agitation: essentially independent of agitation rate; and solids concentration: essentially independent up to approximately 20% solids (treating higher solid containing solutions may be possible, but were not investigated during this study).

Experimental results have shown that two waste products can be effectively treated by the leach lime roast process, i.e., excess sulfuric acid is neutralized, and metal values are recovered from waste smelter slag. The recovery of the metal

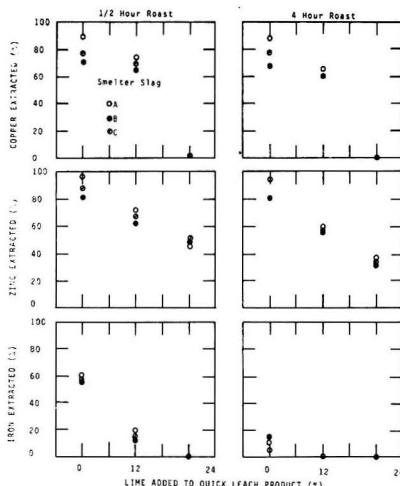


Figure 12. Comparison of metal extractions from three smelter slags with respect to roast time and lime content: water leach

values provides an economic incentive for use of this process over the lime neutralization process.

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# Reactivity Scale for Atmospheric Hydrocarbons Based on Reaction with Hydroxyl Radical

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■ By use of relative and absolute rate constants for the reaction of the hydroxyl radical (OH) with a number of alkanes, alkenes, aromatics, and ketones, a reactivity scale is formulated based on the rate of removal of hydrocarbons and oxygenates by reaction with OH. In this five-class scale, each class spans an order of magnitude in reactivity relative to methane. Thus, assigned reactivities range from  $<10$  for Class I (containing only methane) to  $>10^4$  for Class V containing the most reactive compounds (e.g., *d*-limonene). This scale differs in several significant ways from those presently utilized by air pollution control agencies and various industrial laboratories. For example, in contrast to other scales based on secondary manifestations such as yields of ozone and eye irritation, it focuses directly on initial rates of photooxidation. The proposed scale also provides a clearer understanding of the importance of alkanes in the generation of ozone during periods of prolonged irradiation. The present scale can be readily extended to include additional organic compounds (e.g., natural and anthropogenic hydrocarbons, oxygenates, chlorinated solvents), once their rate of reaction with OH is known.

It has been recognized for many years (1–21) that all hydrocarbons occurring in polluted atmospheres are not equally effective in producing photochemical oxidant, and hence that the application of cost effective strategies for the control of hydrocarbons requires that more stringent emissions reductions be applied to the more reactive organic compounds (22–25). This in turn has led to a continuing requirement for a rational assessment of hydrocarbon reactivity as a basis for control decisions. Such an assessment is particularly critical since attainment of the Federal air quality standard for photochemical oxidant has been sought largely through the stringent control of hydrocarbon emissions (26–27).

The first effort to formulate and apply a practical hydrocarbon reactivity scale was taken in 1966 with the implementation by the Los Angeles Air Pollution Control District (LAAPCD) of a regulation, known as Rule 66, to limit solvent organic emissions on the basis of their capacity for promoting photochemical smog formation (24–25). This rule and other conceptions of reactivity scales (28) represented a major advance in the application of the information then available concerning the mechanisms of photochemical smog formation to the development of practical air pollutant emission control strategies.

Not surprisingly however, both in the past and present, there have been significant differences in hydrocarbon reactivity scales proposed by local, regional, and national air pollution control agencies (23, 29–31) as well as by industry (14, 16). As shown in Table I, this can lead to very large differences in emission inventory estimates and in approaches to hydrocarbon control (29, 32, 33). In this case, reactive hydrocarbon emission inventory levels calculated by Goeller et al. (32) using hydrocarbon reactivity definitions of the Environmental Protection Agency (EPA) on the one hand, and the California Air Resources Board (ARB) and LAAPCD on the other, differed by factors of 3 to 4!

A second problem common to virtually all previous reactivity classifications has been their reliance on smog chamber data obtained for relatively short irradiation (~2–6 h) periods.

Thus, the recent concern over oxidant formation resulting from longer irradiations during pollutant transport to regions downwind of urban sources introduces additional difficulties both in defining what constitutes a reactive hydrocarbon and in categorizing degrees of reactivity. For example, a compound such as propane, the major component in liquefied petroleum gas (LPG) and often cited as a “clean” fuel, is now known (34–36) to contribute to the formation of photochemical oxidants in the later stages of day-long irradiation periods. However, on the basis of data obtained during short-term irradiations, propane has been classified as “unreactive” in a reactivity scale proposed (23) by B. Dimitriadis of the EPA (hereafter referred to as the EPA reactivity scale).

Altshuler and Bufalini (9, 17) have reviewed the various definitions of hydrocarbon reactivity and summarized results of numerous studies up to 1970. The criteria used for evaluating hydrocarbon reactivity include hydrocarbon consumption, the conversion of nitric oxide to nitrogen dioxide, ozone formation, aerosol formation, eye irritation, and plant damage. It is generally agreed that the criteria most suitable with respect to photochemical oxidant control strategies are ozone dosage or maximum ozone concentration (29). However, establishing a definitive hydrocarbon reactivity scale to be applied specifically to the control of ozone formation requires an extensive and lengthy experimental program in which the ozone-forming capability of each individual hydrocarbon is determined under simulated atmospheric conditions, including long-term irradiation (i.e., 12–14 h).

An alternative basis for assessing hydrocarbon reactivity, which would appear to have considerable utility and a valid experimental foundation, is the formulation of a reactivity scale based on the rate of disappearance of hydrocarbons due to reaction with the hydroxyl radical, the key intermediate species in photochemical air pollution.

## Results and Discussion

It is only in the last six years that the critical role of OH in photochemical smog formation has been generally recognized (37–40) and that appreciable rate constant data have become available for the reaction of OH with several classes of hydrocarbons. The importance of OH as a reactive intermediate relative to species such as  $O_3$ ,  $O(^3P)$ , and  $HO_2$  has been shown previously (39–41) through computer modeling of smog chamber data. For example, Niki et al. (39) showed that the reactivity of a number of hydrocarbons, as measured by the rate of conversion of NO to  $NO_2$ , correlated significantly better with OH rate constants than with either  $O(^3P)$  or  $O_3$  rate constants.

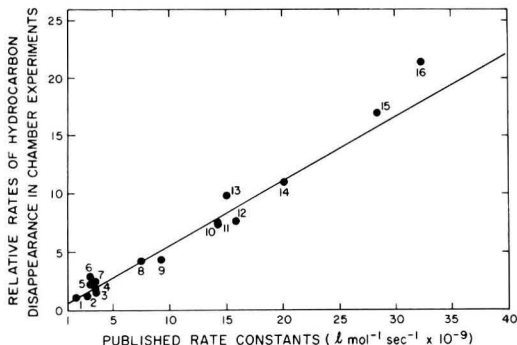
**Table I. Comparison of Reactive Hydrocarbon Inventory Levels for Fixed Sources Under Alternative Reactivity Assumptions (from Ref. 32 Based on Pre-1973 Data)**

Control strategy	Reactive hydrocarbons, tons/day		
	Consistent EPA	ARB-LAAPCD	Rand Corp.
1970	876.0	228.3	636.3
1975 nominal	427.3	102.2	239.9
1975 maximal	290.6	57.7	129.9

The utility of a large environmental chamber in obtaining relative rate constants with an accuracy of  $\pm 20\%$  for the reaction of the hydroxyl radical with a variety of hydrocarbons was demonstrated in an earlier study in this laboratory (41). This method has recently been extended to an investigation of more than a dozen additional hydrocarbons, including seven compounds for which OH rate constants are not currently available. The detailed kinetic data derived from this investigation have been reported elsewhere (42). In these studies we determined the relative rates of disappearance of selected alkanes, alkenes, and aromatic hydrocarbons under simulated atmospheric conditions of temperature, pressure, concentrations, light intensity, and other trace contaminants ( $\text{NO}_x$ , CO, hydrocarbons, water). These relative rate constants were placed on an absolute basis using the published rate constants for OH + *n*-butane. The assumption that OH was responsible for the hydrocarbon disappearance under the experimental conditions employed (41) was subsequently supported by the very good agreement between OH rate constants determined for the individual compounds using flash photolysis-resonance fluorescence techniques (43, 44) and those obtained in the initial chamber study (41). The general validity of the chamber method for obtaining OH rate constants is illustrated in Figure 1 where the good correspondence between chamber values (41, 42) and the available literature values [(45) and references in Table IV] is shown graphically.

The importance of the chamber method for the purposes of formulating a reactivity scale is the simultaneous determination of valid rate constants for reactions of OH with a large number and wide variety of atmospherically important hydrocarbons. This substantially expands the number of compounds which can be incorporated, now and in the near future, in the resulting reactivity scale. In this regard we are currently extending (46) the chamber method to the determination of rate constants for reactions of OH with natural hydrocarbons, such as terpenes, and solvent hydrocarbons, such as ketones and chloroethenes, for which no data currently exist. Preliminary kinetic data (46) for selected natural hydrocarbons and ketones are included in our proposed reactivity scale.

**Use of OH Rate Constants as a Reactivity Index.** From the successful correlation of OH rate constants with the rates of hydrocarbon disappearance observed in our chamber simulations, we conclude that, to a good approximation, this



**Figure 1.** Comparison of relative rates of hydrocarbon disappearance determined by environmental chamber method (refs. 41 and 42) with selected published rate constants (cited in Table IV) for reaction of those hydrocarbons with OH radicals

Line shown represents one to one correspondence and has slope of  $(1/1.8) \times 10^{-9} \text{ mol s l}^{-1}$ . Compounds shown are: 1, *n*-butane; 2, isopentane; 3, toluene; 4, 2-methylpentane; 5, *n*-hexane; 6, ethene; 7, 3-methylpentane; 8, *p*-xylene; 9, *o*-xylene; 10–11, *m*-xylene; 12, 1,2,3-trimethylbenzene; 13, propene; 14, 1,2,4-trimethylbenzene; 15, 1,3,5-trimethylbenzene; 16, *cis*-2-butene

**Table II. Effect of 0.1 PPM Ozone on Calculated Lifetimes of Selected Alkenes Based on Reaction with OH Radicals ( $1 \times 10^7$  Radicals/cm<sup>3</sup>)<sup>a</sup> at 300 K**

Alkene	OH rate constants, <sup>b</sup> $\text{l. mol}^{-1} \text{s}^{-1}$	Half-life <sup>c</sup> for $[\text{O}_3] = 0, \text{ h}$	Half-life <sup>d</sup> for $[\text{O}_3] = 0.1 \text{ ppm, h}$
Ethene	$3.8 \times 10^9$	3.0	2.8
Propene	$1.5 \times 10^{10}$	0.76	0.67
<i>cis</i> -2-Butene	$3.2 \times 10^{10}$	0.36	0.20
1,3-Butadiene	$4.6 \times 10^{10}$	0.25	0.24

<sup>a</sup> Concentration used in these calculations—see text. <sup>b</sup> See references in Table IV. <sup>c</sup>  $t_{1/2} = 0.693/k_{\text{OH}}[\text{OH}]$  under the assumption of attack only by OH. <sup>d</sup>  $t_{1/2} = 0.693/(k_{\text{OH}}[\text{OH}] + k_{\text{O}_3}[\text{O}_3])$ ;  $k_{\text{O}_3}$  taken from refs. 45 and 59.

correlation can be extrapolated to the atmosphere for alkenes in ambient air parcels during the early morning hours when ozone levels are generally quite low ( $\leq 0.05$  ppm), and for alkanes and aromatics at essentially all times and locations. The latter assumption, namely, that an OH rate constant is a good "reactivity index" for alkanes and aromatics throughout an irradiation day (or multiple irradiation days), rests upon the fact that the rates of reaction of these classes of hydrocarbons with species such as ozone,  $\text{O}(\text{^3P})$  atoms, and hydroperoxyl radicals are several orders of magnitude slower than with OH (45, 47–49). For example, even at the highest ozone concentrations experienced in ambient atmospheres,  $\text{O}_3$  will not contribute significantly to the photooxidation of alkanes and aromatics.

This is in contrast to the case for alkenes which, although the rate constants for reaction of  $\text{O}_3$  with alkenes are not particularly large (45), react rapidly with ozone at the average concentrations commonly encountered in polluted ambient air ( $\sim 0.1$ – $0.2$  ppm). The approximate magnitude of the effect of ozone on the atmospheric lifetimes of alkenes is given in Table II. From their OH rate constants (see Table IV), atmospheric lifetimes for four alkenes were obtained by assuming an OH radical concentration in polluted atmospheres of  $10^7$  radicals  $\text{cm}^{-3}$ , which is a reasonable value on the basis of both model calculations (50) and recent atmospheric measurements (51–53). The half-life given in column 3 of Table II is defined as  $t_{1/2} = 0.693/k(\text{OH})$ , and assumes depletion of the hydrocarbon solely by the hydroxyl radical. When one assumes an average concentration of 0.10 ppm of  $\text{O}_3$ , the more reactive alkenes show considerably shorter half-lives (column 4). For example, the lifetime of *cis*-2-butene in the atmosphere is 0.36 h assuming only reaction with OH, but this is reduced to 0.20 h when reaction with  $\text{O}_3$  at a concentration of 0.1 ppm is considered.

**Proposed Reactivity Scale.** Under the assumption that hydrocarbon depletion is due solely to attack by OH (with the qualification noted for alkenes), we propose a five-class reactivity scale based on hydrocarbon disappearance rates due to reaction with OH. The ranges of reactivities for the five proposed classes each span an order of magnitude in reactivity relative to methane and are shown in Table III. The hydrocarbon half-lives, as defined above, are also shown for each reactivity range.

Hydroxyl radical rate constant data for a wide range of atmospheric hydrocarbons have been taken from the literature as well as from our own studies and are compiled and referenced in Table IV. The assignment of these compounds in the various classes of our proposed reactivity scale is shown in the last column of Table IV. For interest, carbon monoxide is included in this table since, although it is not a hydrocarbon, it is present in polluted urban atmospheres but is generally regarded as being "unreactive" in ambient air. Thus, carbon

monoxide appears as being somewhat reactive in Class II, which also includes ethane and acetylene. In our current compilation of compounds, methane is the only compound listed which appears in Class I, and 2-methyl- and 2,3-dimethyl-2-butene and *d*-limonene are the only compounds in Class V. Several of the higher alkenes and 1,3-butadiene appear at the upper end of Class IV. Data from our recent study of monoterpene hydrocarbons (46) indicate that many of these compounds will appear in Class V (54).

**Comparison with Other Scales.** The ranking of reactivities for the aromatic hydrocarbons in our scale is essentially the same as that obtained by Altshuller et al. (4) and by Kopczynski (7, 17). Although our proposed scale is based solely on hydrocarbon disappearance rates, Altshuller and Bufalini (17) have shown that this measure of reactivity is very similar to the one based on nitric oxide oxidation rates. They showed that the ranking of reactivities of hydrocarbons from the nitric oxide photooxidation studies of Altshuller and

Cohen (6) and Glasson and Tuesday (8) was essentially the same as that obtained from the studies of hydrocarbon consumption carried out by Schuck and Doyle (1), Stephens and Scott (3), and Tuesday (5). We are currently investigating methods of quantitatively relating hydrocarbon consumption to nitric oxide oxidation and ozone formation, the parameter of greatest interest in formulating control strategies for oxidant reduction.

As indicated above, Rule 66 formulated by the LAAPCD in 1966 represented the first hydrocarbon control measure based on photochemical reactivity. Although this regulation has been effective, results from recent studies (34-36) indicate that the 4-6 h irradiations (25), from which assignments of the degree of reactivity of hydrocarbons were made in formulating Rule 66, did not give sufficient recognition to the ozone-forming potential of slow reactors such as *n*-butane and propane. Consequently, it is now realized that measures more stringent than Rule 66 are necessary to achieve reductions in ozone formation to levels approaching those mandated by the U.S. Clean Air Act Amendments of 1970.

Recognition of such deficiencies in current hydrocarbon control regulations has led to reexamination of present hydrocarbon reactivity classifications. The focus of these re-evaluations has been the five-class reactivity scale (see Table V) proposed by B. Dimitriadis at the EPA Solvent Reactivity Conference in 1974 (23). Significant changes have been suggested for this reactivity classification by the California ARB (29, 30), the LAAPCD (31), the EPA (55), and by industry. However, since no final conclusions have been reached by any of these agencies at this time, we will restrict comparison of our proposed scale to the 1974 EPA scale.

**Table III. Reactivity Scale for Hydrocarbons Based on Rate of Disappearance of Hydrocarbon Due to Reaction with Hydroxyl Radicals**

Class	Half-life <sup>a</sup>	Reactivity rel to methane (= 1)
I	>9.9 days	<10
II	24 h to 9.9 days	10-100
III	2.4-24 h	100-1000
IV	0.24-2.4 h	1000-10 000
V	<0.24 h	>10 000

<sup>a</sup>  $t_{1/2} = 0.693/k_{OH}[OH]$ .

**Table IV. Proposed Reactivity Classification of Hydrocarbons and CO Based on Reaction with Hydroxyl Radicals**

Compound	$k_{OH} + \text{Cpd} (\text{l. mol}^{-1} \text{s}^{-1}) \times 10^{-9}$	Ref <sup>a</sup>	Reactivity rel to methane	Proposed class, see Table III
Methane	0.0048	(60)	1	I
CO	0.084	(45)	18	II
Acetylene	0.11	(45, 61, 66)	23	II
Ethane	0.16	(62)	33	II
Benzene	0.85	(43, 44)	180	III
Propane	1.3	(63)	270	III
<i>n</i> -Butane	1.8	(41, 42)	375	III
Isopentane	2.0	(42)	420	III
Methyl ethyl ketone	2.1	(46)	440	III
2-Methylpentane	3.2	(42)	670	III
Toluene	3.6	(43, 44)	750	III
<i>n</i> -Propylbenzene	3.7	(42)	770	III
Isopropylbenzene	3.7	(42)	770	III
Ethene	3.8	(42, 64-66)	790	III
<i>n</i> -Hexane	3.8	(42)	790	III
3-Methylpentane	4.3	(42)	900	III
Ethylbenzene	4.8	(42)	1000	III-IV
<i>p</i> -Xylene	7.45	(41, 43)	1530	IV
<i>p</i> -Ethyltoluene	7.8	(42)	1625	IV
<i>o</i> -Ethyltoluene	8.2	(42)	1710	IV
<i>o</i> -Xylene	8.4	(41, 43)	1750	IV
Methyl isobutyl ketone	9.2	(46)	1920	IV
<i>m</i> -Ethyltoluene	11.7	(42)	2420	IV
<i>m</i> -Xylene	14.1	(41, 43)	2920	IV
1,2,3-Trimethylbenzene	14.9	(41, 43)	3100	IV
Propene	15.1	(67)	3150	IV
1,2,4-Trimethylbenzene	20	(41, 43)	4170	IV
1,3,5-Trimethylbenzene	29.7	(41, 43)	6190	IV
<i>cis</i> -2-Butene	32.3	(67)	6730	IV
$\beta$ -Pinene	42	(46)	8750	IV
1,3-Butadiene	46.4	(42)	9670	IV-V
2-Methyl-2-butene	48	(68)	10 000	V
2,3-Dimethyl-2-butene	67	(69)	14 000	V
<i>d</i> -Limonene	90	(46)	18 800	V

<sup>a</sup> Where more than one reference is cited, an average value is given for the rate constant.

**Table V. Proposed EPA Reactivity Classification of Organics (from Ref. 23, 1974)**

Class I, nonreactive	Class II, reactive	Class III, reactive	Class IV, reactive	Class V, reactive
C <sub>1</sub> -C <sub>3</sub> paraffins	Mono-tertiary-alkyl benzenes	C <sub>4+</sub> paraffins	Primary and secondary alkyl benzenes	Aliphatic olefins
Acetylene	Cyclic ketones	Cycloparaffins	Dialkyl benzenes	$\alpha$ -Methyl styrene
Benzene	Tertiary-alkyl acetates	Styrene	Branched alkyl ketones	Aliphatic aldehydes
Benzaldehyde	2-Nitropropane	<i>n</i> -Alkyl ketones	Primary and secondary alkyl alcohols	Tri- and tetra-alkyl benzenes
Acetone		Primary and secondary alkyl acetates	Cellosolve acetate	Unsaturated ketones
Methanol		<i>N</i> -methyl pyrrolidone	Partially halogenated olefins	Diacetone alcohol
Tertiary-alkyl alcohols		<i>N,N</i> -dimethyl acetamide		Ethers
Phenyl acetate		Partially halogenated paraffins		Cellosolves
Methyl benzoate		Partially halogenated paraffins		
Ethyl amines				
Dimethyl formamide				
Perhalogenated hydrocarbons				
Reactivity rating: 1.0	3.5	6.5	9.7	14.3

Briefly, the EPA has proposed, on the basis of previous experimental studies, that methane, ethane, acetylene, propane, and benzene are essentially nonreactive for typical urban ambient hydrocarbon-NO<sub>x</sub> ratios (23) and these compounds are placed in Class I on their scale. Three other classes have been proposed for mobile source hydrocarbon emissions (56)—Class III (C<sub>4</sub> and higher alkanes), Class IV (aromatics less benzene), and Class V (alkenes). When stationary source hydrocarbons, including solvents (Class II), are added to the list, five classes are suggested as shown in Table V.

The reactivity classification proposed here (Tables III and IV) can be compared with that suggested by the EPA (Table V). It is evident that several significant differences emerge:

- The C<sub>1</sub>-C<sub>3</sub> alkanes are given equal weighting in the EPA scale, and all are designated unreactive, whereas our scale clearly differentiates among the three compounds from methane in Class I and ethane in Class II to the more reactive propane in Class III.
- According to our proposed classification, benzene and *n*-butane are of similar reactivity, whereas the EPA scale places them in Class I and III, respectively.
- All the alkenes are placed in Class V of the EPA scale, whereas our proposed scale shows a differentiation in reactivity from ethene in Class III to 2,3-dimethyl-2-butene in Class V.
- Our scale gives recognition to the high reactivity of natural hydrocarbons such as  $\beta$ -pinene and *d*-limonene, placing these in Class IV and V, respectively. The present published EPA scale does not give a classification for natural hydrocarbons, although they could be loosely categorized as substituted alkenes in Class V.

In addition to noting these differences, some similarities exist between the two scales. For example, our scale shows that 1,3-butadiene is highly reactive which is consistent with previous studies indicating it to be a facile precursor of eye irritants (17) and highly effective in producing oxidant during irradiation of HC-NO<sub>x</sub> mixtures (57). Also, methanol would appear in the low half of Class II in our scale based on a recent determination of the rate constant for OH attack on methanol (58). The value found was  $k_{(\text{OH}+\text{CH}_3\text{OH})}/k_{(\text{OH}+\text{CO})} = 0.63$  at 298 K. This reduces to  $5.3 \times 10^7 \text{ l. mol}^{-1} \text{ s}^{-1}$  based on  $k_{(\text{OH}+\text{CO})} = 8.4 \times 10^7 \text{ l. mol}^{-1} \text{ s}^{-1}$  (45). Hence, both our scale and the EPA's show methanol to be relatively unreactive.

It should be emphasized that the classification proposed in our scale is not strictly applicable to compounds which

undergo significant photodissociation in the atmosphere, for example, aliphatic aldehydes. In such cases, the compound will be more reactive than predicted from a scale based on hydrocarbon depletion due solely to OH attack. However, our proposed classification emphasizes that most compounds react in polluted atmospheres and suggests that the Class I scale be reserved only for the few compounds which have half-lives greater than about 10 days.

#### Conclusion

Our proposed reactivity scale based on the depletion of hydrocarbons by reaction with the OH radical has utility in assessing hydrocarbon chemical behavior in polluted ambient air. Since only those organic compounds which participate in atmospheric reactions are of consequence in the chemical transformations in ambient air, their relative reactivity toward OH is a useful and directly measurable index of their potential importance in the production of secondary pollutants.

One advantage of the proposed scale is that, because it is based on the individual rate constants for hydrocarbon reaction with OH, any degree of gradation in reactivity may be used to formulate any desired number of classes—from relatively few to a large number of classes or even an ordered ranking of compounds. A second strength of the present scale is that it can be readily extended to include additional organic compounds once their rate of reaction with OH is known. Finally, the proposed scale gives greater weight than previous reactivity scales to the alkanes and a number of aromatic hydrocarbons, which require a longer period of time to react but can contribute significantly to ozone formation during longer irradiation periods, e.g., during their transport downwind from urban centers—a phenomenon of increasing concern to air pollution control agencies.

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# Chemical Dynamics of a Polluted Watershed, the Merrimack River in Northern New England

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■ A time series of the major-ion and nutrient composition of the Merrimack River has been obtained at several locations on the main channel over a one-year period. Combination of the chemical data with the flow allows chemical mass fluxes to be calculated, and the major chemical inputs modeled. Sodium, calcium, magnesium, and potassium show significant anthropogenic input (greater than 50%) as well as natural input; phosphate is predominantly anthropogenic while silicate is predominantly natural. The dependence of concentration on flow can be modeled for some constituents using two input components. The first component has a constant mean composition and steady flux, and is identified as groundwater and sewage, while the other component has a mean composition which is flow dependent, and is identified with runoff events.

The chemistry and geochemistry of rivers can be understood only if they are studied as dynamic systems: It is the fluxes of dissolved constituents rather than their concentration levels which indicate the response of a watershed to seasonal effects and pollution. The flux of a given constituent can be determined directly from time series of its concentration and associated water flow. The flux is, in principle, the resultant of many diverse processes acting in the watershed. In some instances these processes may be deduced from examination of the data but in general they can be identified only by using additional information about the geology, rainwater composition, land use, population distribution, and pollution load of the catchment area. These various factors can be parameterized and incorporated in a hydrochemical model of the system.

Only a few published attempts have been made to construct dynamic chemical flux models, and these have been restricted to small natural systems (1-7). In an attempt to extend this approach to an urbanized, polluted stream, an 18-month time series of chemical concentrations has been made at 20 stations distributed throughout the Merrimack River Basin in New Hampshire and Massachusetts. Data from nine of these stations along the main channel are used in the present discussion (Figure 1).

The Merrimack is the fourth largest river in New England with a drainage basin of 12 310 km<sup>2</sup>. The river descends 825 meters in a course of 270 km. Over the period sampled, rainfall averaged 113 cm/yr. Daily discharge at the most downstream gauging station, Lowell, averaged 240 m<sup>3</sup>/s ranging from more than 1075 m<sup>3</sup>/s in the spring to less than 10 m<sup>3</sup>/s in the autumn. The lower 35.4 km of the channel are tidal (8). The first significant urban development is at Concord about halfway down the river. Thereafter a series of manufacturing centers and associated urban areas line the stream to its estuary at about Plum Island. Table IV names these centers and itemizes their waste inputs (9-11).

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## Methods

Stations were located to monitor the influences of major features—large tributaries, towns, dams, etc. Where possible they were placed adjacent to USGS automatic gauging stations. Ideally, samples should be collected from midstream. This was not generally feasible and so water was taken from the banks in regions of active flow. The stations were occupied at irregular intervals of about four weeks, and the data for the period June 1971 to August 1972 will be discussed.

Of the species analyzed, Na, K, Mg, and Ca were determined by flame atomic absorption; phosphate and silicate colorimetrically (12); and chloride by specific ion electrode using internal additions. Examples of these data for stations 4 and 15 appear in Figure 1.

## Interpretation of Data

Two models are developed in this paper. The first one models fluxes to identify sources in the river system. The second model treats concentration vs. flow. The first model can be used in explaining features seen in the second.

## Chemical Mass Fluxes

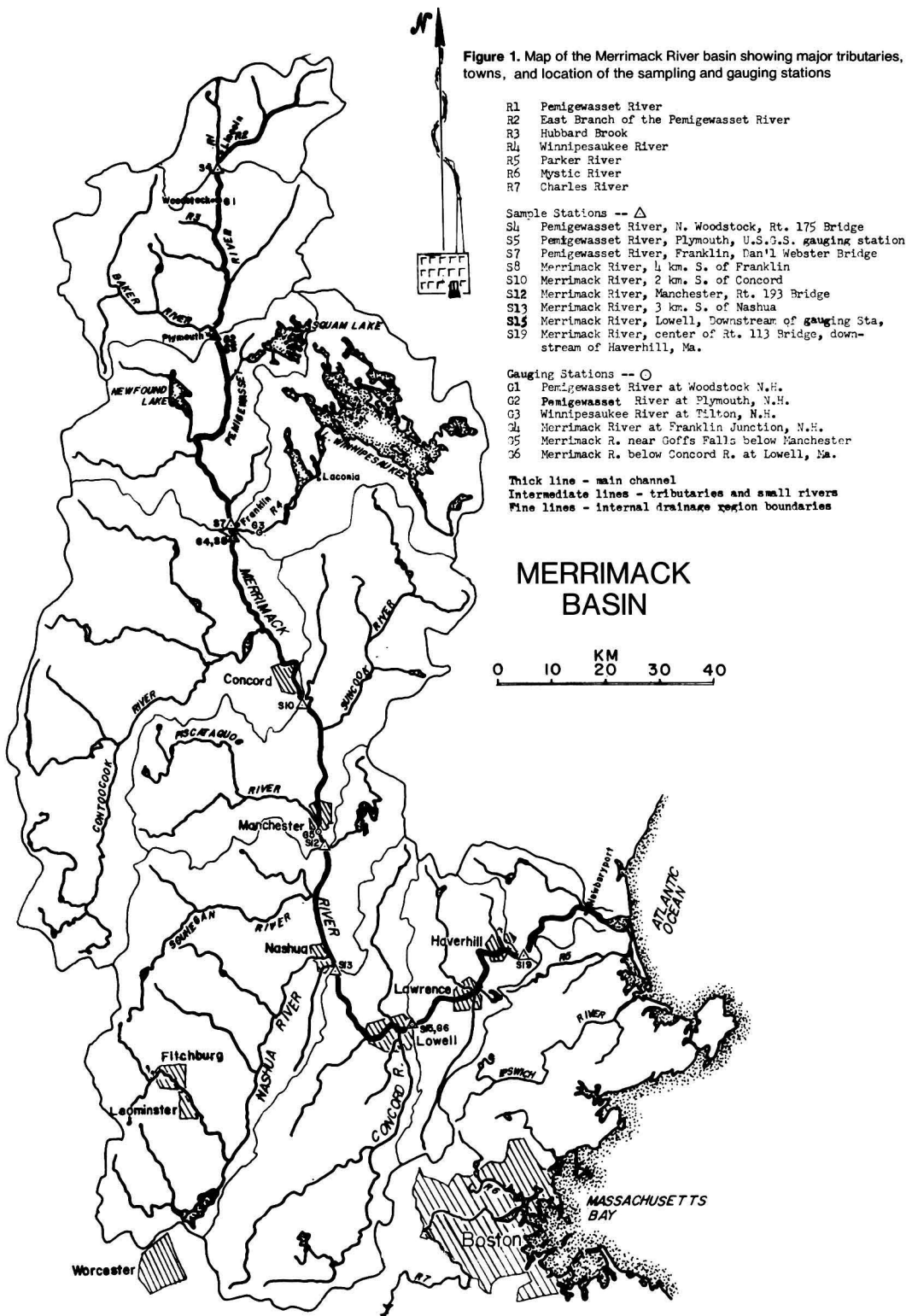
Many sources to a river system are areally distributed: weathering of rocks; precipitation; agricultural runoff; and many forms of urban and suburban waste. The Merrimack Basin was divided into regions (Figure 1) (Table I) large enough to allow a quantitative description of the fluxes through each region and from the sources within each region using available data. All data from a region were normalized by the region's drainage area. This simplifies the comparison and interpretation of our data.

Water fluxes were calculated from U.S. Geological Survey gauging station data (USGS unpublished). Since in the lower reaches of the river, weirs modulate flow in diurnal and weekly cycles, the flow data have been averaged over several days around the sampling date. For stations where flow was not monitored, an estimate was made from plots of flow vs. area drained. This was regarded as unjustifiable for the upstream stations that were therefore not included in the flux calculations.

The chemical mass flux data were obtained as the averaged product of concentration and flow (Table VI). The chemical flux averages for the sampling dates were taken to approximate the annual averages, since the sample date average of

Table I. Areal Data

Station #	Area drained, km <sup>2</sup>	Incremental area, km <sup>2</sup>	Population density, no./ km <sup>2</sup>
4	464	0-4	464
5	1610	4-5	1146
7	2670	5-7	1060
8	3910	7-8	1240
10	6330	8-10	2320
12	8020	10-12	1690
13	10499	12-13	2479
15	11958	13-15	159
19	12606	15-19	642



water fluxes was close to the annual average (Table II). Further corrections to the data were felt to be unjustified. In the few cases where data points were missing, the concentrations were interpolated linearly between data from adjacent stations and sampling dates.

**Table II. Regional Precipitation and Runoff**

This table compares the sample date average runoff fluxes of water normalized by area (cm/yr), for each of the basin regions, with the same data monitored bihourly for an annual period within the sample period. In the right column, the annual period runoff is compared with precipitation for the same period. Precipitation is from NOAA data (13)

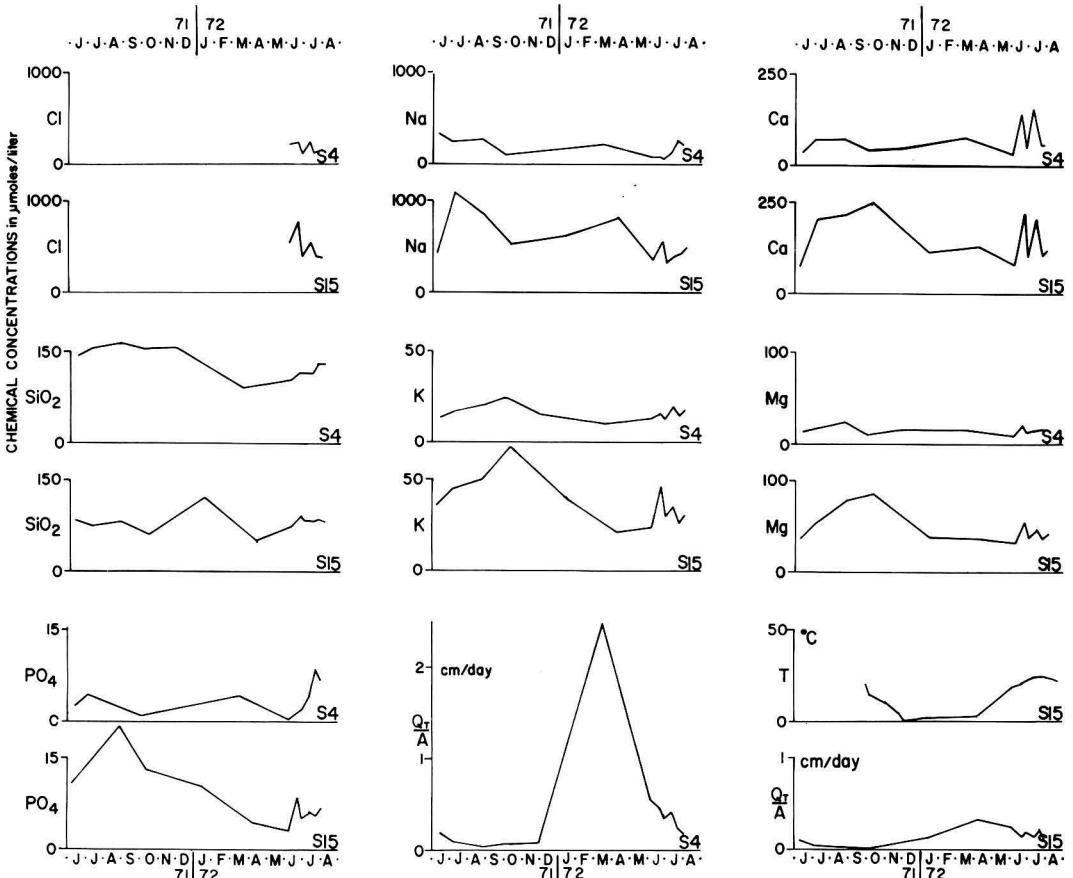
Region between stations	Runoff/area averaged for dates sampled	Runoff/area, 8/71-7/72	Precipitation, 8/71-7/72	(Runoff/area)/precipitation $\times 100$
0-4	154.1	89.6	105.7	85%
4-5	32.3	66.4	99.1	67%
5-7	29.7	60.2	112.6	53%
7-8	42.8	49.2	107.0	46%
8-10	37.3	53.6	102.5	52%
10-12	52.9	53.6	102.5	52%
12-13	58.8	64.8	114.3	57%
13-15	58.8	64.8	114.3	57%
15-19	58.8	64.8	114.3	57%

In order to understand mechanisms controlling river chemistry it is important to separate the chemical mass flux of each dissolved constituent into the most important source components. These sources can be accounted for in terms of processes. One can divide the chemical sources into three broad categories—*atmospheric*, *weathering*, and *anthropogenic*. These sources are interrelated but are useful as classifications. The atmospheric source (Table III) is represented

**Table III. Atmospheric Input, Kmol/Km<sup>2</sup>/Yr**

Na<sup>+</sup> and Cl<sup>-</sup> are adjusted for ocean effects, all other inputs are assumed constant (9, 14, 15)

Region	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	C <sup>-</sup>	SiO <sub>2</sub>	PO <sub>4</sub> <sup>3-</sup>
0-4	6.3	16.6	5.24	4.61	8.2	~0	0.5
4-5	6.3	16.6	5.24	4.61	8.2	~0	0.5
5-7	6.3	16.6	5.24	4.61	8.2	~0	0.5
7-8	6.6	16.6	5.24	4.61	8.5	~0	0.5
8-10	6.6	16.6	5.24	4.61	8.5	~0	0.5
10-12	7.6	16.6	5.24	4.61	9.8	~0	0.5
12-13	7.9	16.6	5.24	4.61	10.4	~0	0.5
13-15	10.1	16.6	5.24	4.61	13.3	~0	0.5
15-19	10.4	16.6	5.24	4.61	13.5	~0	0.5



**Figure 2.** Sample upstream and downstream plots of time series of data used in this discussion. The plots of flow are in cm/day; temperature is in degrees centigrade; and concentration is in  $\mu\text{moles}\cdot\text{liter}^{-1}$

**Table IV. Waste Input (M<sup>3</sup>/S)**

These are best estimates compiled from the available data (9-17)

	Lincoln, N. Woodstock, N.H.	Woodstock, N.H.	Plymouth, N.H.	Tilton, N.H.	Franklin, N. H.	Concord, N.H.	Manchester, N.H.	Nashua, N.H.	Fitchburg-Leominster, Clinton, Mass.	Greater Lowell, Mass.	Concord River towns	Greater Lawrence	Haverhill, Mass.	Lowell, Lawrence, Haverhill, Mass.	Total
Plastics							0.011		0.033						0.044
Food processing							0.025	0.110	0.004					0.009	0.147
Metal plating								0.013	0.017						0.030
Pulp and paper						0.020		0.013	0.697					0.496	1.226
Dairy														0.004	0.004
Rendering														0.005	0.005
Textiles							0.077							0.057	0.134
Wool							0.007							0.058	0.065
Tanning					0.0018	0.053	0.026	0.044						0.007	0.132
Miscellaneous								0.013	0.035						0.049
Industrial total					0.0018	0.073	0.146	0.193	0.786	0.180		0.284	0.162	0.636	1.836
Municipal		0.04	0.11		0.1985	0.271	0.610	0.495	0.500	0.798	0.136	1.284	0.399	2.616	4.843
Total wastes		0.04	0.11		0.2003	0.344	0.756	0.688	1.286	0.977	0.136	1.568	0.561	3.252	6.679

**Table V. Anthropogenic Input (Cm/Yr) Normalized to Area**

These data are condensed from Table IV and, together with the population data in Table I represent the complete set of data on anthropogenic input used in the flux analysis (9-17)

Region between stations	Total waste	Municipal waste	Industrial waste	Paper waste	Wool & cotton	Wool & cotton tanning & rendering
0-4	<sup>a</sup>	0	<sup>a</sup>	<sup>a</sup>	0	0
4-5	0.110	0.110	<sup>a</sup>	<sup>a</sup>	0	0
5-7	<sup>a</sup>	0	0	0	0	0
7-8	0.790	0.785	0.005	0	0	0.005
8-10	0.448	0.353	0.095	0.026	0	0.069
10-12	1.411	1.139	0.272	0	0.157	0.205
12-13	2.512	1.267	1.246	0.904	0	0.056
13-15	2.409	2.020	0.389	0.747	0.174	0.192
15-19	10.514	8.273	2.241			

<sup>a</sup> No data were available to estimate these inputs but they are considered to be negligible in these regions.

**Table VI. Average Chemical Flux/Area Data and Model**

Units are kmol km<sup>-2</sup> yr<sup>-1</sup>. These are the data to which the flux model was fitted. Model results follow the data

Region between stations	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SiO <sub>2</sub>	PO <sub>4</sub>
0-4	274	121.5	23.4	21.3	238	165.4	0.61
4-5	63	28.3	13.4	5.9	151	25.8	0.40
5-7	86	40.6	9.7	6.0	193	31.0	-0.16
7-8	124	47.7	12.3	8.2	123	30.7	0.20
8-10	251	46.5	19.3	10.6	369	19.5	0.49
10-12	232	49.3	17.3	17.1	295	39.8	2.71
12-13	217	77.3	22.5	12.4	246	46.4	0.36
13-15	565	133.5	48.9	45.8	723	46.6	3.75
15-19	1802	313.8	102.4	72.5	2118	52.3	5.81
Results of Model							
Per capita input, kilo mol/person yr		2.84 ± 0.35 <sup>a</sup>	0.454 ± 0.051	0.161 ± 0.024	0.116 ± 0.024	3.41 ± 0.51	— <sup>b</sup> 0.0065 ± 0.0026
Concentration background input μmol/l.		141 ± 108	75 ± 16	17 ± 7	15 ± 7	154 ± 156	95 ± 14
Concentration background input μmol/l.		141	75	17	15	154	95
Concentration of textile mill inputs μmol/l.		— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup> 1080 ± 460
Correlation coeff.		0.994	0.997	0.992	0.987	0.991	0.986 0.989

<sup>a</sup> 95% confidence interval. <sup>b</sup> The inclusion of this parameter does not significantly improve the model fit.

by precipitation and fallout materials collected on an open sampler. This is certainly an underestimate due to the very efficient scavenging effects of vegetation (1). (In this discussion this deficit appears as weathering.) Rainfall compositions were taken from Junge (14) and total atmospheric fluxes from Fisher et al. (2) and Pearson and Fisher (15). Weathering processes yield material derived from the chemical attack of rain- and groundwater on soils and rocks. This is treated as an unknown in the following model. The anthropogenic sources include both rural and urban sewage, industrial sewage and waste, and fertilizer (Tables IV and V). Data for amounts and compositions of sewage and industrial effluents were taken from the Army Corps of Engineers and other sources (9-11).

#### Flux Model

The net regional mass flux per unit area for a chemical component ( $F_R/A$ ) is modeled as the sum of the component mass fluxes:

$$F_R/A = \frac{F_{atm}}{A} + \frac{F_w}{A} + \sum_i \frac{C_{ai} \cdot Q_{ai}}{A} \quad (1)$$

$F_{atm}$  refers to fluxes of atmospheric and  $F_w$  to weathering derived materials.  $C_{ai}$  and  $Q_{ai}$  are the concentration and water fluxes from each of  $i$  anthropogenic components.

The parameters that could be estimated were used as model constraints, and the remaining unknowns were determined using least squares fitting.  $F_R/A$  is presented in the chemical input Table VI.  $F_{atm}/A$  was taken from the data in Table III. The anthropogenic parameters used in the model were selected by graphical comparison between possible inputs (Tables I and V) and chemical flux/area data (Table VI), assuming chemical fluxes were proportional to water fluxes or to population.

Population density alone was sufficient to give a good fit for all species but phosphate and silicate. The phosphate model included both population density and a component from the textiles, cotton, and tanning industries. Silicate required no anthropogenic inputs. The combined inputs of weathering and atmospheric sources were treated as proportional to the regional water input from runoff ( $Q_R/A$ ) (Table II). This we call the background input, subscript  $b$ .

$$F_b/A = C_b Q_R/A = F_w/A + F_{atm}/A \quad (2)$$

$C_b$  is the concentration of inputs less terrestrial anthropogenic inputs. The model using this expression for background inputs yielded much better fits than if the combined chemical weathering and atmospheric input rates were treated as constant or as proportional to rainfall. This is seen most clearly for silica.

A correlation between annual runoff and background chemical fluxes/areas does not require a direct relationship between the two. Atmospheric chemical input is relatively constant so variations in background must be due to weathering related processes. Since the rainfall in the basin is relatively uniform (Table II), variations in annual runoff are attributable to variations in the rates of evaporation and transpiration which are in turn related to topography, vegetation, etc. Topography and vegetation will also affect weathering rates, but not necessarily through effects on runoff. In this basin the effects on runoff and weathering are highly correlated. Table VI, bottom, and Figure 3 summarize the model and results.

The model chemical flux/area values for the summed natural components are compared in Table VII with the data from Hubbard Brook (16) which drains part of the region between stations 4 and 5. The values for Ca and K are quite similar but the model Mg flux is low. The Na data are significantly higher than any of the reported annual averages. It is

**Table VII**

Mass flux per unit area: water flux times weathering concentration ( $Q_r \cdot C_w$ ), kmol km<sup>-2</sup> yr<sup>-1</sup>

	Na	Ca	Mg	K
Hubbard Brook av (13)	30	30	12	4.4
Region 4-5	46	24	6	4.8
Region 5-7	42	22	5	4.4

**Table VIII. Per Capita Production and Use (17)**

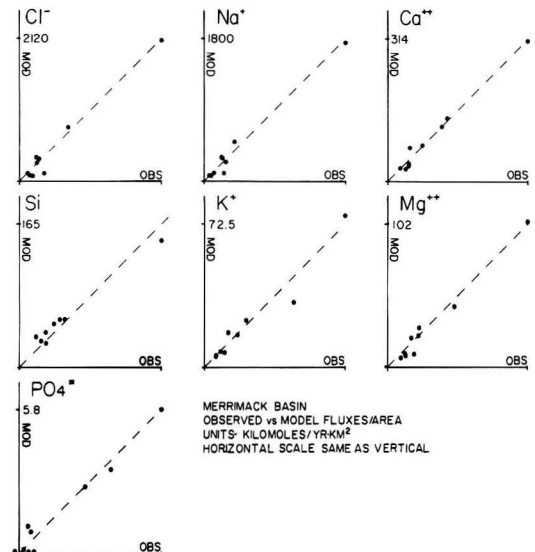
	Kmol yr <sup>-1</sup>		Kg yr <sup>-1</sup>	
	US	C7	US	C7
Na	3.6	2.8	83	65
Ca	1.8	0.45	70	18
Mg	0.11	0.16	2.6	3.9
K	0.26	0.12	10.2	4.7

likely that this is due to the road-salting of Routes 3 and 93 which parallel the main channel through this area.

Table VIII compares the calculated per capita release of Na, Ca, Mg, and K in the Merrimack Basin with the yearly national production data (17).

#### Interpretation of Flux Model

The major identifiable pollution source is road salt. Contamination of ground and well waters is a serious problem in Massachusetts. An average of 107 metric tons km<sup>-2</sup> of salt is applied annually in the conurbation around Boston and between 39 and 63 metric tons km<sup>-2</sup> yr<sup>-1</sup> in the suburban areas (18). The mass flux data indicate that about 100 metric tons km<sup>-2</sup> yr<sup>-1</sup> of sodium as NaCl is being injected between stations 15 and 19. This is almost certainly derived from road salt and is a minimum value since calcium is also a significant although highly variable component. While this source is probably the major one for Na, Ca, and Cl, others such as fertilizer, food, and building and industrial materials must also contribute significantly. The dominant phosphate source appears to be the wool, cotton, and tanning industries; Their mean effluent composition is 1.1 m mol/l. There is also a small



**Figure 3.** Results of flux model. Vertical (model) scales are same as horizontal (observation) scales. Model results are in Table VI



population-related component of about 6 mol per capita per year.

The only obvious anthropogenic sources of silica are minor components in soaps and in conditioners in textiles. Since the silica content of precipitation is negligible, weathering must be the main supply, and indeed the flux data show a strong correlation with water flux alone. There is an insignificant human input of silica. During the year, silica shows a temporal variation negatively correlated with temperature, a possible indicator of biological uptake. Because of the distribution and quality of the data, the effect of this factor on the silica distribution cannot be resolved. A similar problem affects interpretation of phosphate data.

#### Flow Model

There is an obvious relationship between concentration and flow (Figure 2), and a model was investigated relating these parameters. Hydrographs can be interpreted in terms of two components, the apparent background flow which is low and relatively constant and "runoff events" which are superimposed upon it. The background of baseflow includes groundwaters of long and short residence times and, in urban areas, the sewage flow. In the Merrimack Basin, these components have quite constant composition and a low, stable flow. It is therefore plausible to model the total chemical flux (subscript  $T$ ) in terms of two components, one of constant mean com-

position (subscript  $c$ ), and the other with a runoff-dependent mean composition (subscript  $v$ ) (19-21).

$$Q_T = Q_c + Q_v \quad (3)$$

$$Q_T C_T = Q_c C_c + Q_v C_v \quad (4)$$

where  $Q$  and  $C$  signify water flux and species concentration. The runoff dependent concentration,  $C_v$ , can be modeled as a first order function of the runoff flow.

$$C_v = C_{v1} + C_{v2} \cdot Q_v \quad (5)$$

The field measurements are of  $Q_T$  and  $C_T$ : either  $Q_c$  or  $Q_v$  must be determined to solve for  $C_c$ ,  $C_{v1}$ , and  $C_{v2}$ . Because the baseflow includes water from recent runoff events and because sewage flow is relatively steady,  $Q_c$  is taken to be intermediate between a constant minimum flow and the observed baseflow.

$$Q_c = \alpha(Q_B - Q_{Bmin}) + Q_{Bmin} \quad (6)$$

where  $Q_B$  is the baseflow at a given time derived from the hydrograph,  $Q_{Bmin}$  is the minimum observed baseflow at that location on the river, and  $\alpha$  is a constant  $0 \leq \alpha \leq 1$ . As  $\alpha$  tends to zero,  $Q_c$  approaches a component of constant flux and composition; as  $\alpha$  goes to unity,  $Q_c$  becomes identical to the baseflow. When we combine Equations 1, 2, and 3:

$$C_T = C_c Q_c + (C_{v1} + C_{v2}) Q_v / Q_T \quad (7)$$

**Table IX**

Results of concentration-flow model calculation. Chemical units are  $\mu\text{m l}^{-1}$ . The number of sample points used in the calculation is shown as # Points;  $r$  is the correlation coefficient, actual vs. model prediction;  $C_v$  is  $(C_{v1} + Q_c C_{v2})$  averaged for the sampling dates and is included for comparison with  $C_c$  since the data did not always constrain the

values for  $C_{v1} + C_{v2}$ ;  $\alpha$  is the best value determined for the station. Column  $p(r=0)$  is an estimate of the likelihood that the model results are noncorrelated,  $r=0$ , with the real system. Greater than 1% is not considered good

Station no.	# Points	$C_c$	$C_{v1}$	$C_{v2}$ Na	$r$	$\overline{C_v}$	$\alpha$	$p(r=0)$
4	12	259	98	48	0.48	167	0.1	10
5	12	314	162	-14	0.58	156	0.1	5
7	12	384	107	274	0.59	159	0.1	5
8	10	411	59	593	0.60	157	0.1	5
10	11	611	93	1245	0.48	274	0.2	10
12	11	890	93	971	0.86	208	0.2	0.5
13	11	755	338	553	0.68	259	0.2	5
15	12	766	617	1650	0.57	345	0.3	5
19	12	855	1177	3685	0.61	524	0.3	5
Station no.	# Points	$C_c$	$C_{v1}$	$C_{v2}$ K	$r$	$\overline{C_v}$		$p(r=0)$
4	12	23.3	13.6	-1.4	0.77	12.6		0.5
5	12	15.6	20.3	-12.9	0.50	15.3		10
7	12	25.2	11.9	11.3	0.59	14.1		5
8	11	26.5	10.5	19.5	0.65	13.4		5
10	12	28.1	14.8	20.0	0.70	17.8		1
12	11	46.0	19.7	-17.4	0.88	15.5		0.05
13	12	54.1	18.4	-38.0	0.96	12.5		0.05
15	12	66.2	22.7	-39.1	0.92	16.5		0.05
19	11	67.2	26.6	-61.6	0.86	23.4		5
Station no.	# Points	$C_c$	$C_{v1}$	$C_{v2}$ SiO <sub>2</sub>	$r$	$\overline{C_v}$		$p(r=0)$
4	12	182	114	-11	0.93	98		0.05
5	12	156	114	-71	0.80	86		0.5
7	10	115	94	-9	0.56	95		10
8	12	87	118	-127	0.25	94		25
10	12	71	87	-30	0.23	83		25
12	10	66	94	-57	0.52	83		10
13	11	54	125	-230	0.73	86		1
15	12	51	137	-291	0.76	90		1
19	12	54	114	-158	0.67	89		5

Station no.	# Points	$C_c$	$C_{v1}$	$C_{v2}$ Ca	$r$	$\overline{C_v}$		$p(r=0)$
4	12	39	86	-1	0.28	84		25
5	12	78	40	-17	0.08	83		45
7	12	138	8	380	0.57	82		5
8	11	104	52	282	0.27	97		25
10	11	115	64	370	0.30	104		20
12	12	198	21	328	0.67	70		5
13	12	232	52	116	0.79	72		0.5
15	12	270	63	46	0.73	72		0.5
19	12	259	152	-204	0.65	110		5
Station no.	# Points	$C_c$	$C_{v1}$	$C_{v2}$ Mg	$r$	$\overline{C_v}$		$p(r=0)$
4	12	19.3	13.3	0.9	0.33	12.2		20
5	12	39.2	20.9	0.0	0.82	20.9		0.5
7	12	49.9	10.6	45.5	0.82	19.5		0.5
8	11	45.8	11.9	46.9	0.82	19.0		0.5
10	12	53.9	15.1	79.3	0.79	27.0		0.5
12	12	62.0	26.4	-2.8	0.81	24.3		0.5
13	12	76.1	27.0	-30.4	0.97	21.9		0.05
15	12	90.6	21.4	8.9	0.90	22.9		0.05
19	11	81.6	58.0	99.6	0.86	37.5		0.5
Station no.	# Points	$C_c$	$C_{v1}$	$C_{v2}$ PO <sub>4</sub>	$r$	$\overline{C_v}$		$p(r=0)$
4	11	1.08	0.14	0.10	0.53	0.31		10
5	11	0.44	-0.18	1.43	0.92	0.41		0.05
7	10	0.28	0.03	0.72	0.40	0.18		15
8	11	0.41	0.01	1.11	0.39	0.22		15
10	11	0.52	-0.13	4.83	0.72	0.65		1
12	11	4.10	1.32	-2.13	0.86	0.83		0.5
13	12	4.35	0.94	-3.36	0.88	0.41		0.05
14	12	4.89	2.11	-8.48	0.84	0.99		0.5
15	12	6.40	2.98	-4.48	0.85	1.06		0.05

$$C_T = C_c \left( \frac{Q_c}{Q_T} \right) + C_{v1} \left( \frac{Q_T - Q_c}{Q_T} \right) + C_{v2} \left[ \frac{(Q_T - Q_c)^2}{Q_T} \right] \quad (8)$$

The flow at each station was normalized to the area drained to facilitate intercomparison, and  $C_c$ ,  $C_{v1}$ , and  $C_{v2}$  were determined for each chemical component by a least squares fit to Equation 6. Eleven sets of fits to all chemical parameters were executed, varying  $\alpha$  over the range zero to unity by increments of 0.1. From these, the best value of  $\alpha$  for each station was selected after comparison of the quality of the fits to the different parameters. The likelihood that the resulting model for a particular chemical component was in fact noncorrelated ( $r = 0$ ) with the real system was estimated at each station using a "t-test." This test was applied to the correlation coefficients obtained in the model calculations.

The results of the numerical fits including an average value of the variable compositions ( $C_v$ ) are in Table IX and some examples of the model predictions are in Figure 4. In several instances, due to the small number of data points, a single anomalous data point drastically reduced the quality of the fit. This was especially true for calcium where the model showed at least a 5% likelihood of noncorrelation. The results for sodium were only slightly better. These results are almost certainly due to the seasonal nonflow related input of road salt.

The model results reflect the regionalism of the basin. In the upper basin, potassium, magnesium, phosphate, and silicate generally fit the model well giving values for the "t-test" near 0.5%. In the lower part of the basin, potassium, magnesium, and phosphate gave almost exact fits [ $p(r = 0) \sim 0.05$  to 0.5%], calcium and silica were marginal [ $p(r = 0) \sim 1$  to 5%], and sodium was poor [ $p(r = 0) \sim 5\%$ ]. The best values for  $\alpha$  were 0.1 in the upper and middle sections and 0.2 or 0.3 in the lower basin.

#### Interpretation of Flow Model

This simple mixing model represents many features in the data. The low values for  $\alpha$  indicate the presence of a nearly

constant-rate, constant-composition source for the species studied not equivalent to the baseflow. The generally poor quality of the fits in the middle part of the basin may reflect the increasing complexity of inputs. These include weak anthropogenic sources and a varied array of tributaries each with different residence times and with differences in precipitation and melt-water inputs. The fits improve considerably in the part of the river where a strong and distinct anthropogenic component has developed.

Johnson et al. (19) presented a rather similar flow-concentration model for Hubbard Brook. This model equation is slightly different as is their interpretation of its meaning. In consistent notation:

$$C_T = \frac{C_c - C_v}{1 - \frac{\gamma}{V_0} Q_T} + C_v \quad (9)$$

where  $V_0$  is the volume of groundwater and  $\gamma$  the residence time of the water moving through the system. Equation 2 can be written in the form

$$C_T = \frac{(C_c - C_v)}{Q_T} Q_c + C_v = \frac{C_c - C_v}{1 + \frac{Q_v}{Q_c}} + C_v \quad (10)$$

We differ in equating  $V_0/\gamma$  with  $Q_c$ . At very low input rates  $Q_v$  approaches zero before  $Q_c$  and the ultimate effect is the same.

As in the Hubbard Brook study, we found that  $\text{SiO}_2$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  appear to be diluted with increasing discharge. However our agreement for  $\text{Na}^+$  and  $\text{K}^+$  is poor. This may be an artifact of our much smaller sample size or due to the greater complexity and heterogeneity of the basin studied. It should be emphasized that inputs, particularly of pollutants, are distributed over a wide range of fluxes and compositions.

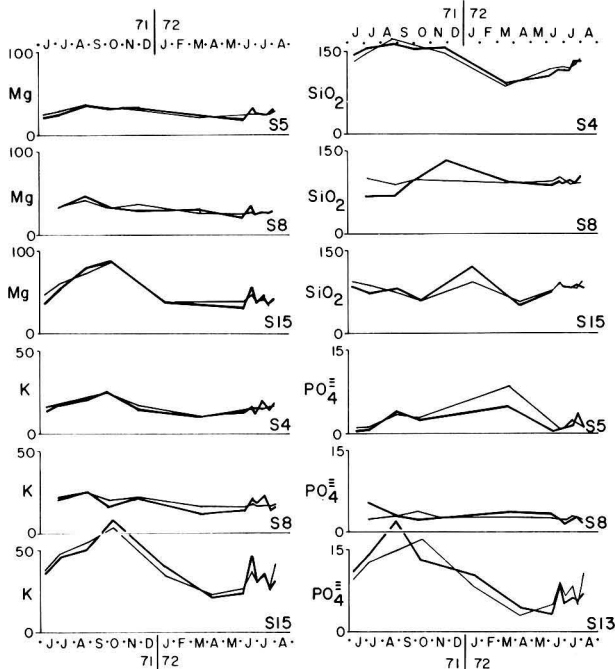


Figure 4. The results of the flow-concentration model (fine lines) compared to the measured values (heavy lines) for selected stations and chemical parameters

**Table X**

Net River fluxes (past station 19) of each parameter, broken into various components (expressed as percentage of total flux). Chemical parameters are in  $10^6 \text{ mol/yr}^{-1}$ , and water is in  $10^6 \text{ m}^3\text{-yr}^{-1}$ .

	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SiO <sub>2</sub>	PO <sub>4</sub> <sup>3-</sup>	H <sub>2</sub> O
(1) Flux at station 19	3960	975	320	231	5060	508	16.4	6420
Percent of station 19 flux from:								
(2) Background ( $C_b \cdot Q_T$ )	22.9	49.4	34.1	41.7	19.5	100	TR <sup>a</sup>	—
(3) Atmospheric ( $Q_{atm}$ )	2.4	21.5	20.6	25.1	2.4	TR	TR	100
(4) Weathering [(2) - (3)]	20.5	27.9	13.5	16.6	17.1	100	TR	—
(5) Anthropogenic [(1) - (2)]	77.1	50.6	65.9	58.3	80.5	TR	100	3.3 <sup>b</sup>
(6) Const. conc. inputs ( $Q_c \cdot C_c$ )	38.7	47.9	46.0	52.5	Si <sup>c</sup>	19.2	70.4	28.1

<sup>a</sup> TR, trace. <sup>b</sup> Effective percentage of water cycled through waste systems. <sup>c</sup> Si, significant.

Hall (20) developed several flow-concentration models one of which (his model 5) is very similar to the one presented here. These models were applied (21) to various rivers including some New England rivers. Hall's results demonstrated the difficulty in selecting an unambiguous model to apply.

All of Hall's models contain an empirical relationship between a storage volume ( $v$ ) in which a complete mixing of inputs occurs, and water flux ( $Q_T$ ) out of that volume:

$$Q_T = kv^n \quad (k \text{ and } n \text{ are constants})$$

Hall's model 5 uses two sources: one of constant concentration  $C_c$  and constant volume  $V_0$ ; the other of constant concentration  $C_v$ , and variable flux  $Q_T$ :

$$C_T = \frac{C_c - C_v}{1 + \frac{K^{-1/n}}{V_0} Q_T^{1/n}} + C_v \quad (11)$$

With the equation in this form, comparison can be made between the denominators of Equations 10 and 11:

$$1 + \frac{Q_v}{Q_c} \quad \text{and} \quad 1 + \frac{K^{-1/n}}{V_0} Q_T^{1/n} \quad (12)$$

An essential difference is that in the model presented here, the denominator is a function of both  $Q_v$  and  $Q_c$  as opposed to  $Q_T$  alone. Our model or an integration of Hall's and ours may be easier to apply on rivers with nonsingle valued flow-concentration relationships. Both denominators approach 1 as  $Q_T$  approaches zero since  $Q_v$  should go to zero faster than  $Q_c$ .

Our data are not sufficient to recommend one of these models. However since the Merrimack concentration data are not single valued with respect to total flow, a method that allows for this was introduced.

### Conclusion

The major sources for the chemical species studied (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, Si, PO<sub>4</sub><sup>2-</sup>) could be described using a flux model. These species could be divided into three classes according to the model. The first group included Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Cl<sup>-</sup>. These species exhibited a significant anthropogenic  $i$  input best correlated with population density and a significant natural input best correlated with runoff water flux. The second class contained PO<sub>4</sub><sup>2-</sup> that showed virtually no natural input, and an additional anthropogenic input from the cotton, wool, and tanning industries. The final class contained silica that showed only a natural input correlated with runoff.

A model of concentration in terms of two components worked adequately only where some feature of the basin simplified the inputs of the chemical species. Thus reasonable results could be obtained for the most northern part of the basin where inputs were almost entirely natural and from a morphologically homogeneous drainage region and for the

southern part of the river basin where anthropogenic inputs dominate the system. In the middle part of the basin the region drained becomes morphologically complex and human inputs are small but significant and, as a consequence, the flow model breaks down.

The flux model, based on more fundamental concepts (mass conservation) than the flow model, provided information even where the flow model failed. Flux models including time-dependent models have much greater potential in unraveling complex river systems such as the Merrimack. Table X presents an integrated interpretation of these results for the Merrimack basin.

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# INDUSTRY TRENDS

**Hach Chemical Co.** is publishing *News and Notes for the Analyst*, a quarterly newsletter to keep customers aware of new analysis and water treatment methods, regulations, and the like, and is asking for comments and suggestions.

**Engineering-Science** (Arcadia, Calif.) will conduct a noise assessment for the California Oil Purification Co., located in Ventura County, Calif.

**Union Camp Corp.** (Wayne, N.J.) has donated 3800 acres, worth \$600 000, to the Nature Conservancy for use as a public environmental studies center. The land is in the Chowan Swamp in northeastern North Carolina.

**Harza Overseas Engineering Co.** (Chicago, Ill.) and Hue Lyew Chin Consulting Engineers (Kingston, Jamaica) will study and make designs for drainage and agricultural development of 10 000 acres of the Black River Upper Morass Area, Jamaica. Ecology will be taken into account.

**American Air Filter Co., Inc.** announced the formation of AAF Lufttechnik GmbH, a subsidiary company that will market AAF products and systems in Germany.

**Northeast Utilities** announced that its Connecticut Yankee Nuclear Power Station was shut down in mid-May for refueling, maintenance, and inspection. The operation took place a bit sooner than scheduled because of a turbine vibration.

**AirPol** (Englewood, N.J.) will provide five venturi scrubber systems for controlling lime sludge kiln emission to International Paper Co., Union Camp Corp., Potlatch Forest Corp., and Kimberly Clark of Canada.

**American Can Co.** (Greenwich, Conn.) announced that U.S. Reduction Co. (East Chicago, Ind.), a producer of recycled aluminum alloys, would become an American Can subsidiary under a \$45 million agreement.

**Geraghty & Miller, Inc.** (Port Washington, N.Y.) has been awarded a \$460 000 EPA contract to monitor groundwater contamination at at least 75 different industrial sites where waste is land disposed.

**Union Carbide Corp.** has dedicated its \$4 million, three-stage Unox wastewater treatment system at its Chemicals and Plastics plant at Marietta, Ohio. The system uses oxygen for secondary treatment; 44 such systems are in operation.

**SUNTECH, Inc.** (Marcus Hook, Pa.), a subsidiary of **Sun Co., Inc.**, is offering a wide range of analytical tests and physical measurements, including environmental testing and tests on petroleum.

**Hamon Cooling Tower Division of Research-Cottrell, Inc.**, has received an order, valued at about \$1.2 million, for design and construction of a mechanical-draft cooling tower for Consumers Power Co.

**Chemico Air Pollution Control Division of Envirotech Corp.**, will supply two venturi scrubbers to Potomac Electric Power Co.'s Dickerson Station to treat flue gases from two 190-MW units.

**Zurn Industries, Inc.**, will relocate its Cooling Tower Division to facilities in Tampa, Fla. Zurn is the licensee of Balcke-Durr of West Germany, the world's oldest cooling tower manufacturer.

**Fluor Engineers and Constructors, Inc.** (Los Angeles, Calif.) will design a 50 000-bbl/day coal liquefaction plant for ERDA under a \$1.9 million contract. The plant will apply advanced technology to Appalachian coal.

## Everybody's bugging you to solve your aluminum smelter's pre-bake oven emissions problem. But who can you bug?

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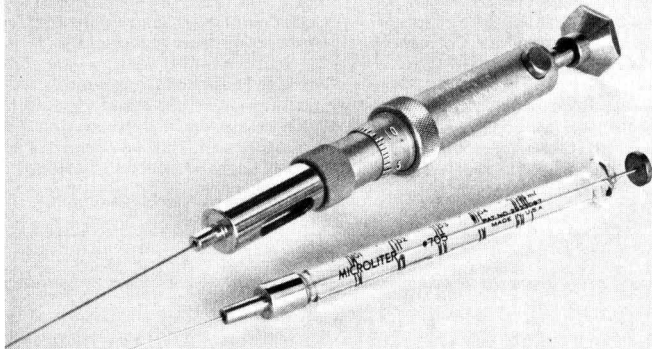


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**BBC Brown Boveri & Co., Ltd.** (Baden, Switzerland) and its member firm, Indústria Elétrica Brown Boveri S.A. (São Paulo, Brazil) will produce turbines and generators, including those for nuclear plants, for the Brazilian Villares Group.

**The Nuclear Energy Liability-Property Insurance Association** (Los Angeles) will refund \$1.6 million to nuclear facility operators. The Association cites an "excellent safety record" as the reason for the premium refund.

**Stone & Webster Engineering Corp.** (Boston, Mass.) is the first engineer-constructor to have a standard (reference) nuclear plant approved by the U.S. Nuclear Regulatory Commission (NRC), the firm announced.

**The Electric Power Research Institute** (Palo Alto, Calif.) has authorized a total of \$55 million for 68 new projects in electric energy research.

**Ford Motor Co.** (Dearborn, Mich.) has a new cupola system for its blast furnace-type steel and iron scrap melter, on which Ford spent \$4.8 million for air pollution control equipment.

**Peabody Engineering** has received orders for over \$4 million worth of Peabody-Holmes "cold" 600 000-cfm electrostatic precipitators from U.S. Steel Corp. Delivery is expected this autumn.

**Hydro Research Science Co.**, a hydraulic engineering firm, has moved into new expanded quarters in Santa Clara, Calif.

**Grumman Ecosystems Corp.** (Bethpage, N.Y.) has received two contracts totaling over \$2.3 million for wastewater treatment facilities at Riviera Beach and West Palm Beach, Fla.

**Hercules Inc.** (Wilmington, Del.) and Tate and Lyle, Ltd. (England) have signed an agreement to develop, make, and market microbial polysaccharides.

**BS&B Industrial Products** (Houston, Tex.) announced completion of a 100 million-scf/day Sulfiban coke oven gas desulfurization facility for Bethlehem Steel Corp. (Bethlehem, Pa.).

**Non-farm business** spent \$6.5 billion for new pollution abatement plant and equipment in 1975, up 17% from 1974, according to the U.S. Department of Commerce.

**The Ceilcote Corp.** (Berea, Ohio) will provide advanced air pollution control equipment, embodying Ceilcote's Ionizing Wet Scrubber, to C-E Globe Refractories, Inc.

**Olson Laboratories, Inc.** (Anaheim, Calif.), an Envirodyne subsidiary, will supply dynamometers for testing motorcycle emissions to EPA's Ann Arbor, Mich., labs. Contract value: About \$164 000.



# NEW PRODUCTS

## Programmed bag sampler

The sequential bag sampler operates unattended for 1-4 days. It is programmed to collect up to 24 ambient air samples in individual bags at selected times. Filled sample bags are returned to a central location for analysis. Environmental Measurements, Inc. 101

## Corrosion inhibitor

The molybdate-bearing corrosion inhibitor/anti-scalant is non-polluting and non-toxic to fish, according to the manufacturer. It is effective over a wide pH range and is recommended for use in recirculating cooling systems. Wright Chemical Corp. 102

## Broken bag detector

Provides continuous on-stack detection and indicates when visible emissions from baghouses or other particulate control devices are emitted. The monitor contains a warning light and an alarm light. Joy Manufacturing Co. 103

## Expansion, waterstop joint

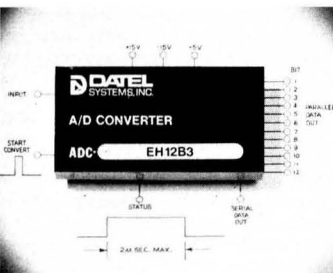
Made of thermoplastic rubber, the joint has been approved by EPA for potable water applications. Sinmast of America, Inc. 104

## Ozone analyzer

Designed for aerial monitoring, the model in a single cycle mode updates data each 10 s and re-references for zero with each measurement. In a multiple cycle mode, updates are each second with a selection of the number of measurements between re-referencing. Dasibi Environmental Corp. 105

## Compactor

Collects and compacts waste in the same 55-gal drum. The compaction force is 3000 psi. The machine occupies 9 ft<sup>2</sup> of floor space. S&G Enterprises, Inc. 106



## A/D converter

The modular analog-to-digital converter performs a 12-bit conversion in 2  $\mu$ s. Input impedance is 1.5 K ohms and, by externally interconnecting pins, the module will accept a unipolar input of 0-10 V or a bipolar input of  $\pm 5$  V. Datel Systems, Inc. 107



## Sea wave analyzer

System to measure, display and record significant wave height consists of a pressure sensor, interconnecting cable and a receiver/computer module. The module contains an analog display, strip-chart recorder and alarm/warning indicators. Bass Engineering, Inc. 108

## Piezoelectric accelerometer

Instrument finds application for monitoring machine vibrations and bearing analysis. The unit has a 100 mV/g output over a frequency range of 1 Hz to 10 kHz. Noise floor is 15  $\mu$ V broadband and amplitude linearity is  $\pm 1\%$  to 15 g. Bolk Beranek and Newman, Inc. 109

## Truck noise measurement kit

The portable kit consists of a sound level motor with an "A"-weighted scale and a measurement range of 60-120 dB; an aluminum tripod; a microphone wind-screen and a calibrator. Edmont-Wilson 110

## Air sampler

This portable sampler counts particles from 0.01-10  $\mu$  or larger, depending on the filter selected. The machine can be used for spot checking or for prolonged testing of air quality. Telstar Electronics Corp. 111

## H<sub>2</sub>S detector

This fixed-installation system digitally displays H<sub>2</sub>S concentrations from 0-99 ppm. The model has high and low alarm circuits that are set by dialing the desired gas levels on switches on the front of the controller. Response time is rapid at temperatures ranging from -40 to 85 °C, according to the manufacturer. Dictaphone Corp. 112

## Suspended solids analyzer

The instrument is designed for secondary, final effluent applications and to monitor other suspended solids concentrations up to 500 ppm. The unit provides continuous, instantaneous measurement with unattended operation. Keene Corp. 113

## Wastewater sampler

The sequential/composite sampler collects from streams and manholes at switch-selected timed intervals from 1-999 min. The sampler can be paced by a flowmeter for flow proportioned collection. Portable or refrigerated models are available. ISCO 114

## Residual chlorine monitor

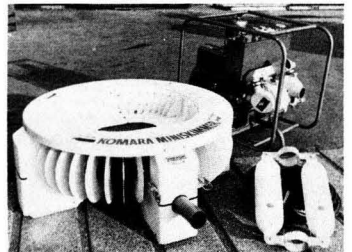
Using iodometric methods, this electrode-based system measures total residual chlorine, including hypochlorite, in acid and alkaline sample streams, over a range of 1000 ppm to less than 0.05 ppm. Orion Research Inc. 115

## Filter

Consists of 34 sheets with 120 ft<sup>2</sup> of filtering area. As a single-stage operation, the filter will remove solids; with the addition of a divider plate, the machine will remove bacteria, yeast cells, cellular debris and fibers, including asbestos, down to 0.1  $\mu$  in size. Star Tank & Filter Corp. 116

## Microbiocide

This microbial control agent, for use in recirculating cooling water, is effective against bacteria, fungi, yeast, mold and algae; it also acts as a corrosion inhibitor. Lonza Inc. 117



## Oil skimmer

This portable, floating, donut-shaped device is suited for spill recovery in large ponds or along shorelines, claims the manufacturer. For heavy crude oil, recovery rate is 10 tons/h; for light diesel fuel, the rate is 2 tons/h. Marine Construction & Design Co. 118

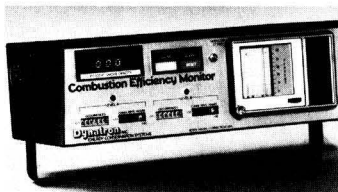
## Air pollution monitoring lab

The mobile unit, designed for on-site monitoring, displays a cab-chassis configuration that can accommodate a wide range of air sampling instruments and a computerized analysis system. Calumet Coach Co. 119

## Automated GC

The manufacturer claims that the gas chromatograph is suitable for rapid, repetitive analysis of low concentrations of almost any specific organic vapor. Carle Instruments, Inc. 120

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#### Opacity monitor

The system is designed to monitor the opacity of visible emissions from boilers, incinerators and process sources. Smoke opacity is displayed as percent or Ringelmann number. Stacks up to 25-ft in diameter can be monitored. Dynatron Inc. **125**

#### Vibration analyzer

The unit reads in units of acceleration, velocity or displacement, and measures level in rms, peak-to-peak or impulse-hold. The portable analyzer measures vibrations down to 0.3 Hz; the meter has selectable time constants. B&K Instruments, Inc. **126**

#### Air pollution monitoring lab

The mobile laboratory contains a self-contained power and water system, cabinets and work surfaces for mounting electronic test equipment and interior lighting. Masts and elevated sampling stacks, via roof access, facilitate testing. Calumet Coach Co. **127**

#### Afterburners

The units, in 13 standard sizes, are designed to thermally destroy odors, smoke and combustible fumes. They have been applied to solve air pollution problems in sewage treatment facilities and in specific industrial processes. Bayco Industries of California **121**

#### Pressurized filter

Features include a diatomite pre-coat tank and backwash separator system, and a closed-loop piping layout that holds solids for recovery of metal fines or the disposal of debris. Xodar Corp. **122**

#### Data logger

Instrument has been adapted to a method 5 EPA train. The logger automatically records time, temperature, velocity pressure, pump vacuum, volume, orifice pressure and leak check parameters without changing the test procedure. The tape and test data are mailed to the company's computer terminal, which furnishes a complete test report. Clean Air Engineering, Inc. **123**

#### Suspended, volatile solids test

Test system includes a digital readout analytical balance, a magnetic filter holder, a desiccator, lab bench drying oven and a muffle furnace. These supplies are required for the EPA-approved Standard Methods gravimetric procedure. Hach Chemical Co. **124**

#### Solar collector

The extruded aluminum tube flattened into a plate allows the manufacture of non-standard, custom-sized panels. The collector is weather resistant and light weight. The collector system is designed to operate in closed systems. Reynolds Metals Co. **128**

#### Hydrogen sulfide analyzer

The unit is a portable, wearable continuous monitor that features an audible alarm that is activated by H<sub>2</sub>S levels beyond a pre-set level. Meter readings are in ppm or in grains. Detection ranges include the low 0-32 ppm range to the high 0-320 ppm range. Energetics Science, Inc. **129**



#### pH recording monitor

The system provides a permanent 30-day record of pH levels in the final water leaving a plant. Two adjustable set points bracket high and low allowable tolerances, while an alarm light and horn indicate variance from the set points. Vari-Systems, Inc. **130**

#### Spectrophotometer

The design of the instrument allows for rapid testing of water, wastes and industrial process fluids. The optics wavelength range is 400-700 nm; the meter has an accuracy of  $\pm 1\%$ . Delta Scientific **131**

#### O<sub>3</sub>, NO<sub>x</sub> calibration system

The portable field calibration system for ozone and oxides of nitrogen uses gas phase titration methods for generating low level concentrations of NO and NO<sub>2</sub>. The ozone generator is temperature controlled and stable. Bendix Corp. **132**

#### Fluorescent microscope

The binocular, wide field, dissecting-type microscope with low magnification power is designed specifically for counting coliform bacteria colonies. Cherne Scientific **133**

#### Sampling valve

The nylon/plastic valve can be attached to either or both ends of a vacuum bottle to obtain a grab sample or pass-through sample of emissions from industrial stacks. No lubricant is necessary and contamination of sample is eliminated. Bethlehem Steel Corp. **134**

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# NEW LITERATURE

**Weatherwatch.** Brochure describes the APTS-3B satellite ground receiving station for monitoring and mapping weather systems. Ask for Bulletin No. M476-125-2.5. Alden Electronic & Impulse Recording Equipment Co., Inc. **151**

**Water purifier.** Flyer sheet describes a residential water purifier that eliminates the need for replacement cartridges and chemical "doping". Water Purification Industries, Inc. **152**

**Pilot chemical facility.** Booklet tells of a pilot chemical facility used to obtain data for designing process plants according to the "zero discharge" concept with no effluent. FMC Corp. **153**

**Water Storage.** Brochure describes the Marolf Strss-Key modular concrete storage tanks for 5000 to several million gal for water or effluent. Ask for Bulletin 16-1183. Marolf, Inc. **154**

**Solids removal.** Bulletin No. KL 4220 discusses advanced concepts in high-rate solids removal from water and wastewater, and gives case histories. Neptune Microfloc Inc. **155**

**Job Safety.** Form 19 lists and describes safety instruments to help to protect employees from potential job hazards. Noise instruments, lifesaving, and emergency oxygen are stressed. Edmont-Wilson **156**

**Wastewater sampling.** Bulletin 9831-A describes automatic, unattended sampler with proportional sampling or constant rate capabilities for domestic and industrial wastewater sampling. FMC Corp. **157**

**Fluid energy control.** Form G147 describes fluid energy control devices that solve pulse and surge problems in piping systems for oil, sewage, chemical, water, fuel, or other applications. Greer Hydraulics, Inc. **158**

**Laboratory ware.** 1976 catalog lists a whole line of plasticware for chemical laboratory use. Ace Scientific **159**

**Portable filter systems.** Technical Bulletin 802 describes low-priced, all-plastic, portable filter systems that can now handle most corrosive liquids, as well as function as a carbon treatment system. Sethco Mfg. Corp. **160**

**pH systems.** Catalog describes improved designs in industrial pH and oxidation-reduction potential (ORP) systems, highlighted by a new self-cleaning line of submersion assemblies and holders. Electrofact **161**

**Liquid sampling.** Data sheet describes Model CG-110 composite sampler and Model DEL-400S discrete/composite liquid sampler. Pro-Tech Inc. **162**

**Ocean acoustics.** Brochure describes line of ocean acoustic transponder releases useful for navigation, offshore wellhead markers, precise positioning, and related applications. InterOcean Systems, Inc. **163**

**Sediment interceptors.** Specification/buyer's guide covers acid-resistant, high-density polyethylene sediment interceptors for drain and waste piping systems and vents. Town & Country Plastics, Inc. **164**

**Gas chromatograph.** Instrument Applications Vol. 10, No. 1/1976 describes new automatic gas chromatograph, and also tells how liquid chromatograph can detect pesticide residues. Varian **165**

**PVC strainers.** Bulletin P-75 describes polyvinyl chloride tubular-element liquid strainers for removing suspended solids to 150  $\mu\text{m}$ . They are corrosion-resistant. Croll-Reynolds Engineering Co. **166**

**Liquid chromatography school.** Publication D27 describes three-day school on practical aspects of liquid chromatography. Waters Associates **167**

**pH meter.** "'76 Products for Science" describes portable pH meter (0.01 or 0.05 readability), oxygen meter, ultrasonic cleaners, and calculators. Other laboratory equipment is listed. Cole-Palmer Instrument Co. **168**

**Vapor recovery.** Bulletin 8-VRL discusses installations of hydrocarbon vapor recovery units. Operations are automatic, and metering and safety systems are included. Edwards Engineering Corp. **169**

**Non-chemical sludge treatment.** Bulletin 400 describes heat treatment process that dewateres sewage sludge without adding chemical conditioners. Costs for 10-60 mgd plants are given. Neptune Nichols **170**

**Slurries.** "Slurry Wall/Trench" describes slurry wall and trench installations that provide watertight cutoffs and prevent waste seepage. Caisson Corp. **171**

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

**Vacuum filtration.** Three booklets describes vacuum filtration, vacuum sludge filters, and vacuum sludge extractors. Technical data are included. Hoffman Filtration Systems **172**

**Wastewater treatment.** Case History C-137 tells how screw bin activators and heavy duty feeders assured an uninterrupted flow of pebble lime and diatomaceous earth for successful wastewater treatment. Vibra Screw Inc. **173**

**Industrial heat pump.** Brochure TP-1 tells about the tempplier heat pump that provides process heat to 230 °F and reclaims waste heat. Westinghouse Electric Corp. **174**

**Bug removal.** Bug Book II gives the latest word on eliminating pests and what pesticide works best for each species. Equipment and applications are covered. West Chemical Products, Inc. **175**

**Sump pumps.** Two catalogs describe submersible sump pumps and domestic sewage pumps. They show installations and cutaway views. F.E. Myers Co. **176**

**Mutant bacteria.** Brochures describe bacteria developed specifically for wastewater treatment and for degradation of hydrocarbons in water. Polybac Corp. **177**

**Water aeration.** Bulletin 502 stresses benefits of company's aeration treatment systems, especially for military use. An effective, economical 3 mgd system was installed at Ft. Chaffee, Ark., in less than 3 wks. Hinde Engineering Co. **192**

**Butterfly valves.** Brochure describes butterfly valves that have Underwriters Laboratories' approval for many applications, including fire fighting. Dover Corp. **193**

**Vapor disposal.** NAO Bulletin 39A describes the MVDU vapor disposal unit that eliminates polluting hydrocarbon vapors from loading terminals. The automatic unit has no smoke, visible flame, or objectionable noise. National Airoil Burner Co., Inc. **194**

**Noise reduction.** Chart No. 115008 gives application data on noise and vibration control systems in industrial, commercial, and institutional environments. Singer Partitions, Inc. **195**

**Forest management.** "Quaking Aspen: Silvics and Management in the Lake States". North Central Experiment Station, Folwell Ave., St. Paul, MN 55108 (write direct).

**Water resources.** Various publications available. Water Resources Research Center, A211 Graduate Research Center, University of Massachusetts, Amherst, MA 01002 (write direct).

**Coastal areas.** Film, "It's Your Coast" is available for free loan. NOAA Motion Picture Service, 12231 Wilkins Ave, Rockville, MD 20852 (write direct).

# BOOKS

**Of Acceptable Risk: Science and the Determination of Safety.** William W. Lawrence. x + 180 pages. William Kaufmann, Inc., One First St., Los Altos, CA 94022. 1976. \$8.95, hard cover; \$4.95, paper.

The first book of its kind, it uses case studies to illuminate and clarify scientific and sociopolitical principles that relate to public safety. It defines and measures various risks, and discusses who decides what risks are acceptable, and on what terms. Among the many subjects covered are exposure to health hazards, pesticide effects, carcinogenesis, and other hazards extant in everyday life.

**Encyclopedia of PVC. Vol. 1.** Leonard I. Nass, Ed. xii + 600 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016. 1976. \$75, hard cover.

This work is the first comprehensive source of scientific and technical information on polyvinyl chloride (PVC) plastics and materials to be published. The first volume discusses PVC degradation and stabilization; stabilization mechanisms; chemically modified PVC; and theory of solvation and plasticization.

**Coal Conversion Technology.** I. Howard Smith and G. J. Werner. xx + 133 pages. Noyes Data Corp., Mill Rd., at Grand Ave., Park Ridge, NJ 07656. 1976. \$24, hard cover.

The conversion of coal to clean fuels is the subject of much discussion at this time, but what is the actual state-of-the-art? This book, originally prepared as an "in-house" report for Millmerran Coal Pty. Ltd. (Brisbane, Australia), discusses more than 100 processes in various stages of development. Among topics emphasized are desulfurization, demineralization, and depolymerization of coal to produce clean, easily-ignitable gaseous or liquid products.

**Concepts of Ecology. 2nd Edition.** Edward J. Kormondy. xiv + 238 pages. Prentice-Hall, Inc., Englewood Cliffs, NJ 07632. 1976. \$9.95, hard cover.

This work covers major ecological concepts, including energy flow, mineral cycling, and growth and regulation of population and communities. It emphasizes structures and functions of ecosystems, especially their homeostatic properties, cybernetic mechanisms, and predictive models. Ecological impact of man's activities is discussed in easily understood terms.

**1976 Energy Fact Book.** 4 parts and 8 appendices. Tetra Tech, Inc., 1911 N. Fort Myer Drive, Arlington, VA 22209. 1976. \$4.95, paper.

Many topics, much of which is presented in tabular and pictorial form, are discussed in this book. Among them are coal reserves, tar sands, oil shale, solar energy, nuclear power, energy legislation, and liquefied coal as a ship fuel. Tetra Tech published this work as part of its support of the U.S. Navy Energy Research and Development Office.

**Fundamentals of Industrial Noise Control.** Lewis H. Bell. 280 pages. Harmony Publications, P.O. Box 52, Trumbull, CT 06611. 1976. \$13.95.

Here is a textbook for the plant or safety engineer who needs to see that his plant meets OSHA noise regulations. Among topics covered are acoustics, acoustical materials and their applications, noise from various types of machinery, monitoring, silencers and mufflers, and other types of control.

**How to do Business with EPA: A Guide to Requirements for Research Grants and Contracts.** 16 pages. Environews, Inc., 1097 National Press Building, Washington, DC 20045. 1976. \$5, paper.

This booklet is intended as a guide to those seeking research contracts and grants from the EPA. It is an unofficial publication; however, EPA Office of Research and Development officials have checked it for accuracy. Research priorities, making applications, solicited and unsolicited proposals, bidder's lists, R&D proposals, and special considerations are among the pertinent topics covered.

**ECOTECHNICS.** 320 pages. Fairchild Books, 7 E. 12th St., New York, NY 10003. 1976. \$50.

This directory lists more than 15 000 European resources in the environmental protection field. These listings offer 820 product classifications in the major environmental areas; i.e., air, water, solid waste, and noise. Full addresses and "Telex" numbers of 5000 consulting firms are given, and resource categories list producers of equipment in the principal areas.

**Nuclear Regulatory Commission: First Annual Report to the President of the United States and Congress.** 200 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. 1976. \$2.70.

This report details the NRC's activities in licensing and regulating nuclear facilities from January 19 to December 31, 1975. It covers safe reactor design, inspection and enforcement, environmental protection, nuclear material control, investigation of abnormal occurrences, standards development, intergovernmental and international cooperation, and response to public concerns.

**Water, Its Effects on Life Quality.** David X. Manners, Ed. 192 pages. Water Quality Research Council, 477 E. Butterfield Rd., Lombard, IL 60148. 1976. \$10, paper.

This book contains proceedings of the 7th International Water Quality Symposium. Its language is such that laymen can understand it. Included are the opinions of many authorities on relationships of water quality to cancer, heart disease, and schizophrenia, water's role in the energy crisis, and water purification effectiveness. Other environmental problems of water quality are also explored by eminent authorities in the field.

**Energy: The Solar-Hydrogen Alternative.** J. O'M. Bookris. xviii + 365 pages. Halsted Press, 605 Third Avenue, New York, NY 10016. 1976. \$27.50, hard cover.

It could be painful if oil and natural gas were exhausted before other energy sources came to the fore, but there is a case for believing that just such a situation may come to pass. However, this book explains how solar-hydrogen alternatives cannot only be devised, but could be competitive with that presently available, and cheaper than energy found in what oil and gas remains in the 1980's. However, the author explains that an effort like the NASA Moon Project would be needed to bring in these alternatives to prevent great dislocations, as well as how such a project should be organized.

**The Solar Generation.** Film, 16 mm, 21 min. Stuart Finley Inc., 3428 Mansfield Rd., Falls Church, VA 22041. 1976. \$35 for rental; \$350 for purchase.

Visit major private and government research laboratories for a behind-the-scenes look at solar cell technology without leaving your seat. See solar homes, thermal plants, thermal electric stations, furnaces, and office buildings worldwide. This film shows the progress made to date in an interestingly presented, easily understandable format.

**Proceedings of the Conference on Environmental Aspects of Chemical Use in Printing Operations.** NTIS accession No. PB 251 401/AS. National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22161. 1976. \$12; \$2.25, microfiche cards.

The conference, sponsored by EPA, was held last September at King of Prussia, Pa.

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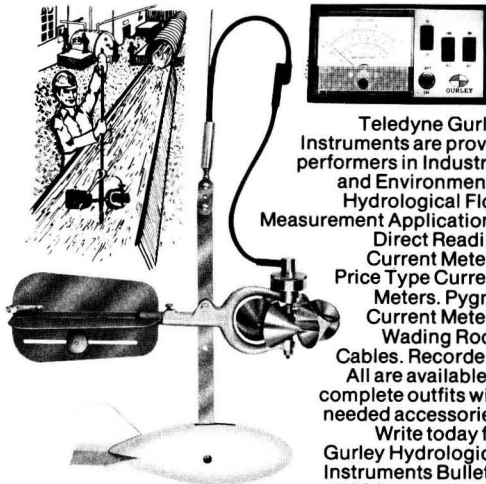
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# MEETING GUIDE

**July 18-21** Denver, Colo.  
**Conference on Land Use and Nuclear Facility Siting: Current Issues.** Atomic Industrial Forum, Inc. (AIF)

*Write:* Conference Department, AIF, 7101 Wisconsin Ave., Washington, D.C. 20014

**July 18-23** Los Angeles, Calif.  
**1976 Intersociety Conference on Transportation.** The American Society of Mechanical Engineers (ASME) and others

*Write:* Gail Jannon, ASME, 345 E. 47th St., New York, N.Y. 10017

**July 25-30** Henniker, N.H.  
**Technology Assessment: Evaluation of Ten Years Experience.** Engineering Foundation

*Write:* Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

**August 1-4** Minneapolis, Minn.  
**31st Annual Meeting.** Soil Conservation Society of America

Theme is "Critical Conservation Choices: A Bicentennial Look." *Write:* Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

**August 1-6** Corvallis, Ore.  
**24th Annual Clay Minerals Conference.** The Clay Minerals Society

*Write:* Dr. W. H. Slabaugh, Dept. of Chemistry, Oregon State University, Corvallis, Ore. 97331

**August 1-6** Rindge, N.H.  
**Tenth Conference on Particle Science and Engineering in the Process Industries.** Engineering Foundation

Conference was previously called Particulate Matter Systems. Attendance is limited to 100. *Write:* Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

**August 2-6** Schenectady, N.Y.  
**Third National Conference on the Effects of Energy Constraints on Transportation Systems.** Union College

*Write:* Office of Graduate Studies and Continuing Education, Wells House, 1 Union Ave., Union College, Schenectady, N.Y. 12308

**August 4-6** Seattle, Wash.  
**1976 Annual Meeting.** American Academy of Clinical Toxicology

*Write:* Barry Rumack, M.D., Rocky Mountain Poison Center, West Eighth and Cherokee Streets, Denver, Colo. 80204

**August 5-6** Sun Valley, Idaho  
**Controlling Airborne Effluents from Fuel Cycle Plants.** American Nuclear Society (ANS)

*Write:* David G. Pettengill, ANS Meetings Manager, ANS, 244 E. Ogden Ave., Hinsdale, Ill. 60521

**August 8-13** Henniker, N.H.  
**4th Conference on National Materials Policy.** Engineering Foundation

Theme is "Engineering Implications of Chronic Resource Scarcity." *Write:* Engineering Foundation Conferences, United Engineering Center, 345 E. 47th St., New York, N.Y. 10017

**August 9-12** Wooster, Ohio  
**Reclamation of Drastically Disturbed Lands.** American Society of Agronomy, U.S. EPA and others

*Write:* Dr. Paul Sutton, Ohio Agricultural Research and Development Center, Route 6, Caldwell, Ohio, or the American Society of Agronomy, 677 South Segoe Road, Madison, Wis. 53711

**August 19-20** New York, N.Y.  
**Energy Conservation in Plants.** New York University's School of Continuing Education

*Write:* Ms. Heidi E. Kaplan, Information Services Manager, Dept. 14NR, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

**August 19-22** Princeton, N.J.  
**1976 Solar Trade Show.** Allied Service Group

*Write:* Allied Service Group, 252 Nassau St., Princeton, N.J. 08540

**August 29-September 3** San Francisco, Calif.

**American Chemical Society's Centennial Meeting.** American Chemical Society (ACS)

Environmental topics will be discussed. *Write:* A. T. Winstead, ACS, 1155 16th St., N.W., Washington, D.C. 20036

**September 7-10** Biloxi, Miss.  
**U.S. Water Resources Council and Interstate Conference on Water Problems (WRC/ICWP) Meeting.** U.S. Water Resources Council and Interstate Conference on Water Problems

*Write:* Jim Fish, assistant secretary treasurer of ICWP, c/o F. Robert Edman and Associates, W-3173 First National Bank Building, St. Paul, Minn. 55101

**September 12-16** Las Vegas, Nev.  
**Annual Convention and Exposition.** National Water Well Association (NWWA)

*Write:* Jay H. Lehr, NWWA, 500 W. Wilson Bridge Rd., Worthington, Ohio 43085

**September 12-17** Oxford, Ohio  
**Emission Sampling for Source Evaluation.** Engineering Foundation

*Write:* Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

**September 12-17** Raleigh, N.C.  
**International Conference on Photochemical Oxidant Pollution and Its Control.** U.S. EPA

*Write:* Mrs. Ernestine McIver, administrative secretary, Triangle Universities Consortium on Air Pollution, P.O. Box 2284, Chapel Hill, N.C. 27514

**September 13-15** Washington, D.C.  
**OCEANS 76.** Marine Technology Society (MTS) and the Institute of Electrical and Electronics Engineers (IEEE) Council on Oceanic Engineering

Environmental topics will be discussed. *Write:* OCEANS 76 Conference Staff, 1730 M St., N.W., Suite 412, Washington, D.C. 20036

**September 13-17** Berkeley, Calif.  
**4th Annual Conference on Nuclear Power and Environmental Assessment.** College of Engineering and Continuing Education in Engineering, University of California-Berkeley

*Write:* Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

## Courses

**July 18-23** Denver, Colo.  
**Process and Environmental Analytical Instrumentation.** Instrument Society of America (ISA)

Attendance is limited to 40. Fee: \$325 (member), \$350 (nonmember). *Write:* R. G. Hand, ISA Short Courses, ISA, 400 Stanwix St., Pittsburgh, Pa. 15222

**July 18-23** Denver, Colo.  
**Sampling and Sample Systems for Process and Environmental Instrumentation.** Instrument Society of America (ISA)

Attendance is limited to 40. Fee: \$325 (member), \$350 (nonmember). *Write:* R. G. Hand, ISA Short Courses, ISA, 400 Stanwix St., Pittsburgh, Pa. 15222

**July 19-23** Chicago, Ill.  
**Applications of Stormwater Management Models.** U.S. Environmental Protection Agency

Fee: \$200. *Write:* Dr. Francis A. DiGiano, Dept. of Civil Engineering, University of Massachusetts, Amherst, Mass. 01002

**July 19-31** Davis, Calif.  
**Man, Energy and the Environment.** University of California Extension

Fee: \$225. *Write:* University of California Extension, Davis, Calif. 95616

**July 20-22** New Brunswick, N.J.  
**Community Noise Control.** Rutgers, The State University of New Jersey/Dept. of Environmental Science

Fee: \$150. *Write:* Robert E. Hague or Donald A. Deieso, Rutgers, The State University of New Jersey, Cook College, Dept. of Environmental Science, P.O. Box 231, New Brunswick, N.J. 08903

**July 26-29** Denver, Colo.  
**Control of Particulate Emissions, Course No. 413.** Air Pollution Training Institute

Fee: \$120. *Write:* Registrar, Air Pollution Training Institute, Research Triangle Park, N.C. 27711

(continued on page 716)

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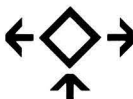
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## MEETING GUIDE (continued)

**July 26-30** Atlanta, Ga.  
**Air Pollution Meteorology, Course No. 411.** Air Pollution Training Institute  
Fee: \$135. Write: Registrar, Air Pollution Training Institute, Research Triangle Park, N.C. 27711

**July 26-30** Columbus, Ohio  
**Modern Methods of Analysis and Protection of Electric Power Systems: Course I. Electric Utility Power Systems.** Ohio State University (OSU)  
Environmental topics will be discussed. Fee: \$300. Write: Mr. Richard D. Frasher, OSU Engineering Short Courses, 2070 Neil Ave., Columbus, Ohio 43210

**August 2-6** Schenectady, N.Y.  
**Third National Conference on the Effects of Energy Constraints on Transportation Systems.** Union College/Graduate Studies and Continuing Education  
Fee: \$350. Write: Sabina Lawrence, institute secretary, Union College, Summer Institute Programs, Schenectady, N.Y. 12308

**August 4-6** Davis, Calif.  
**Communications in Environmental Planning.** University of California Extension  
Fee: \$300. Write: University of California Extension, Davis, Calif. 95616

**August 16-18** Washington, D.C.  
**Energy Conservation, Opportunities and Guidelines for Existing Buildings.** George Washington University  
Fee: \$345. Write: Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

**August 16-20** Madison, Wis.  
**Noise Measurement and Control.** University of Wisconsin-Extension  
Fee: \$325. Write: John M. Leaman, Dept. of Engineering, University of Wisconsin-Extension, 929 N. 6th St., Milwaukee, Wis. 53023

**August 23-24** Madison, Wis.  
**Nuclear Fuel and Waste Management, Course No. 540.** University of Wisconsin-Extension  
Fee: \$110. Write: University of Wisconsin-Extension, 432 N. Lake St., Madison, Wis. 53706

**August 23-27** Appleton, Wis.  
**Water and Waste Water Control.** Institute of Paper Chemistry  
Fee: \$500. Write: Dr. T. A. Howells, Director of Continuing Education, The Institute of Paper Chemistry, P.O. Box 1039, Appleton, Wis. 54911

## Call for Papers

**July 27 deadline**  
**Second Annual Meeting.** American Geophysical Union (AGU) Midwestern Region and the Seismological Society of America (SSA) Eastern Section  
Conference will be held October 21-23 at Ann Arbor, Mich. Write: Meetings, AGU, Suite 1000, 1909 K St., N.W., Washington, D.C. 20006



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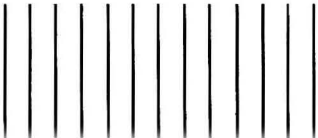
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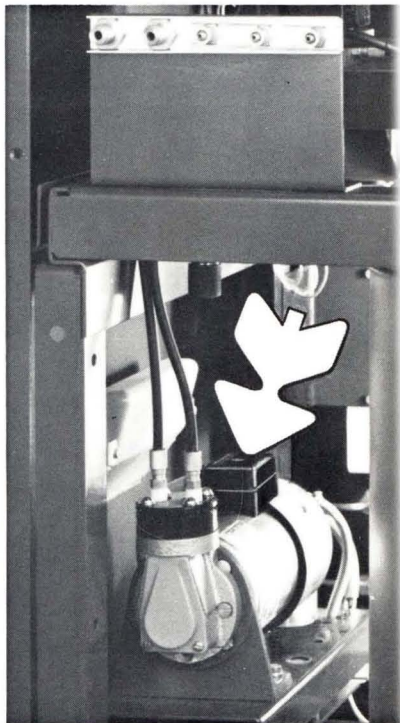
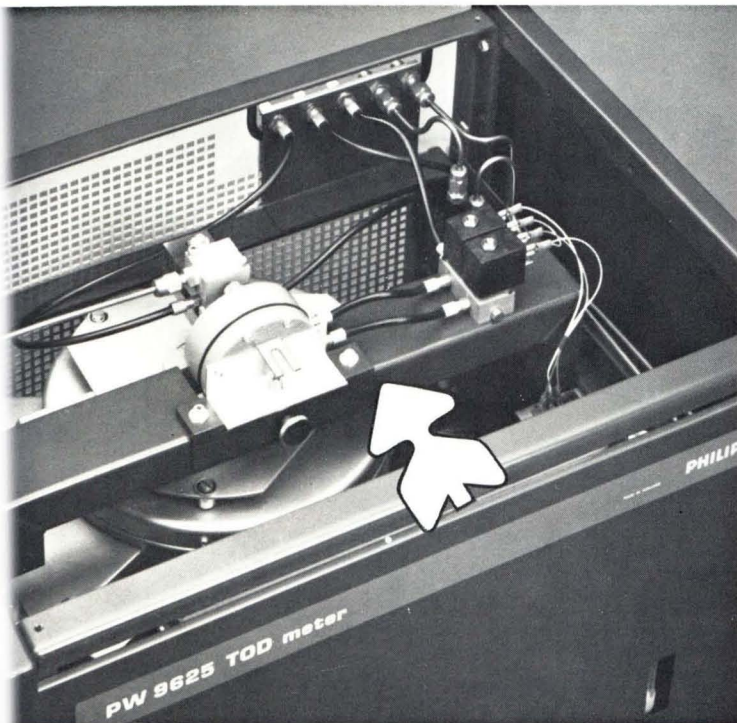
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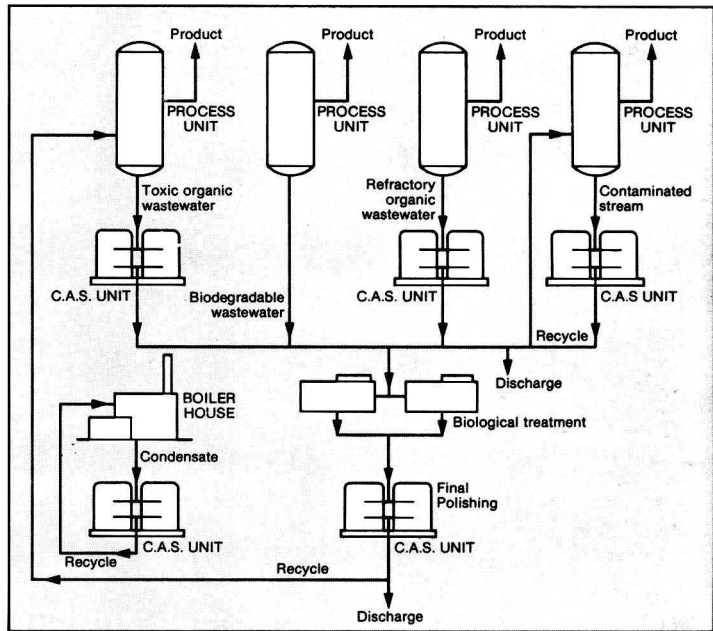
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