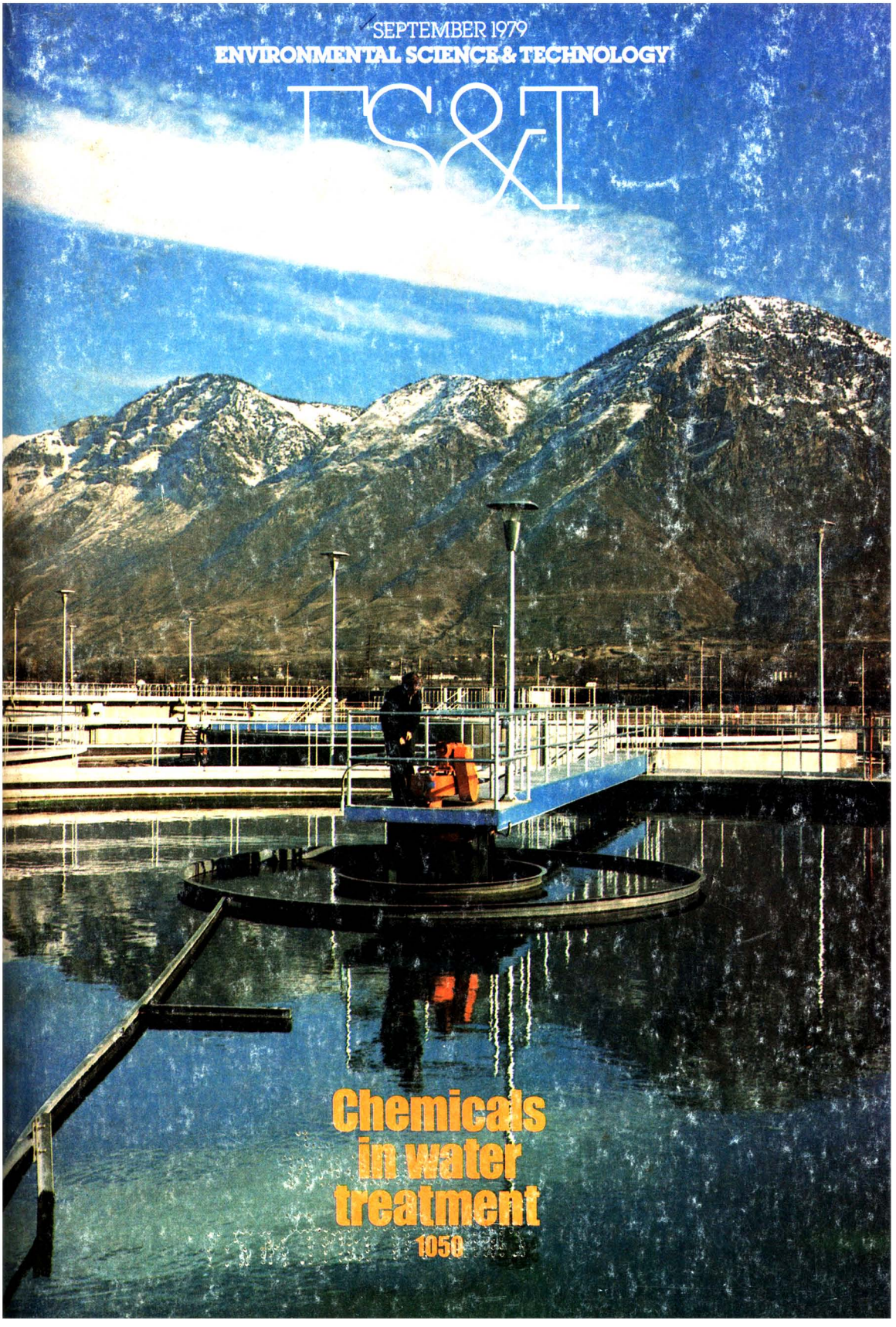
SEPTEMBER 1979
ENVIRONMENTAL SCIENCE & TECHNOLOGY
ES&T



Chemicals in water treatment

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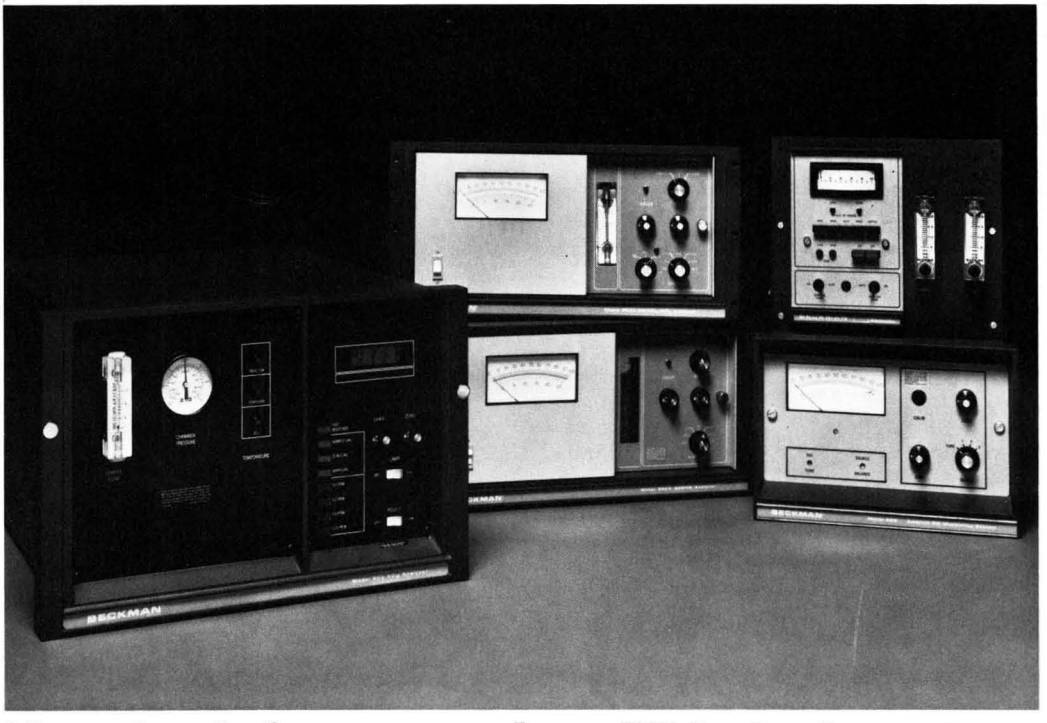

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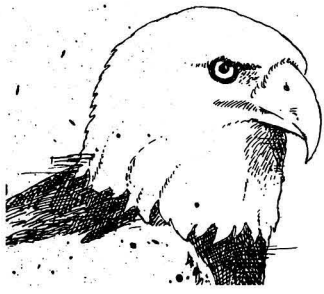

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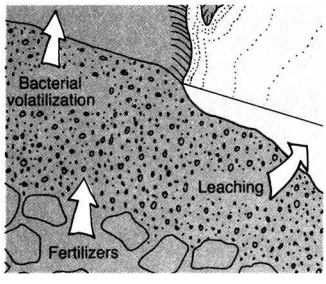

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RESEARCH

Environmental Science & Technology

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CIRCLE 8 ON READER SERVICE CARD

ES&T
GUEST EDITORIAL

Needed: research support

The time has come for the federal government, particularly the U.S. Environmental Protection Agency, to establish an effective program for the support of basic environmental research.

I am aware that in this era of Proposition 13*ism* one is ill advised to promote any new programs, but a partial reallocation of resources is needed at the very minimum. If my observations are accurate, EPA and other agencies are spending precious little of their vast budgets on fundamental environmental research, and I contend that the result is waste . . . waste because protocols are established before analytical schemes or models are appropriately tested; waste because criteria are promulgated without adequate scientific bases; waste due to research done too hastily; waste because attractive alternative methods have to be shunted aside because of the sanctity of work plans and report deadlines.

Of course, I am not blind to the fact that many of EPA's policies are the result of Congressional dictates. Nor am I proposing that EPA assume the responsibility for the support of *all* basic research related to environmental phenomena. Clearly, NSF, USGS, and other agencies also have a responsibility in this area. Equally clear, however, is the need for these agencies to coordinate their programs and, more to the point, for Congress to recognize the need for a well-coordinated fundamental program in environmental research.

Indeed, many hoped that EPA had recognized this need when the center of excellence program was announced. While this program certainly has merit, what is needed more is broad-based support for the scientific community in areas that have long-term promise—and in some cases, no apparent promise at all—for the solution of environmental questions. In a broader sense, what is needed is for the Congress to recognize that research—basic research—is fundamental to the health of our economic system as well as for the preservation of man's natural habitat.

Research properly planned and executed is a good investment of public money. Let us hope that Congress and EPA will continue to evaluate its importance and place basic research at a higher priority position in the federal budget.

Dr. William H. Glaze *is Professor of Chemistry at North Texas State University in Denton, Tex., and former Director of the Institute of Applied Sciences.*

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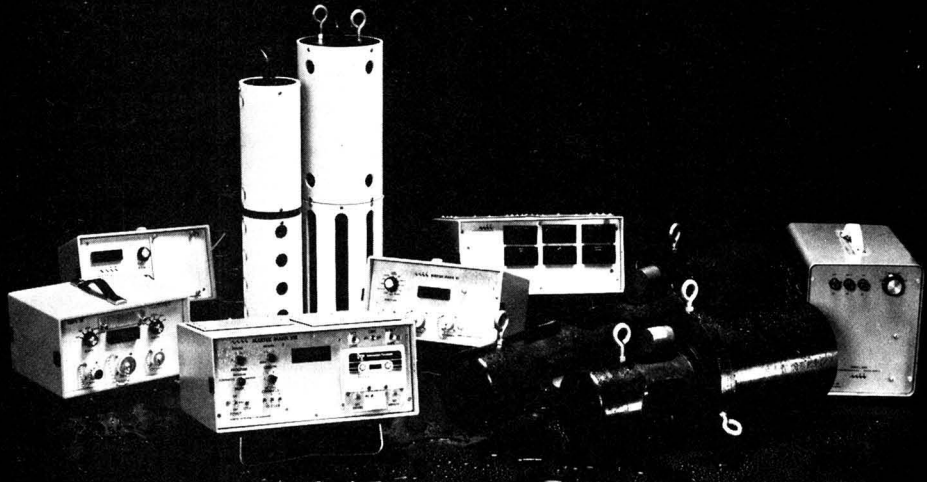

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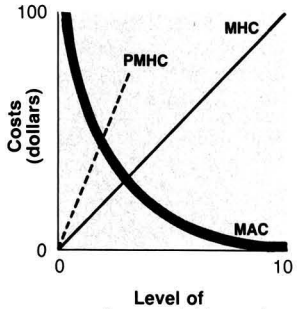
CIRCLE 19 ON READER SERVICE CARD

Health hazards

Dear Sir: I found the article by Professor Jacobs on "Analyzing Environmental Health Hazards" (*ES&T*, May 1979, p 526) to be excellent. It effectively identifies some major concepts which should be thoroughly grasped by policy makers at the legislative and regulatory levels.

Unfortunately, it is difficult to quantify the costs involved. There are the lack of information (scientific, economic, and social), differences in interpretation of existing data, and, even more complex, different perceptions of acceptable risks in the face of uncertainties.

FIGURE 1
Relationships between victims' health costs, polluters' abatement costs, and the level of environmental hazard



In particular, there is one point which should be clarified with regard to Figure 1, redrawn here. Abatement costs are typically exponential, not linear, although major technology changes will make the costs of abatement discontinuous functions. Note that the abatement costs are asymptotic to the ordinate.

Again it is refreshing to read an article which approaches environmental decisions on a more rational basis.

John A. Roth
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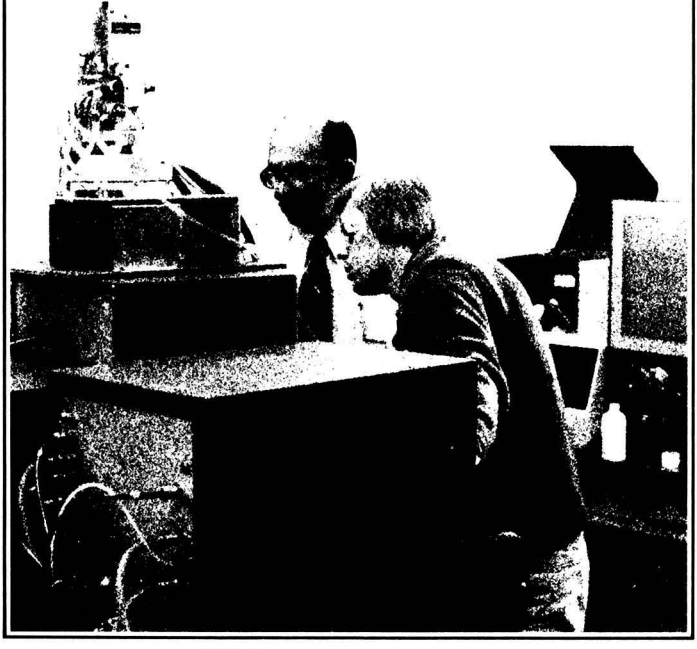

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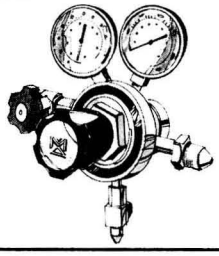

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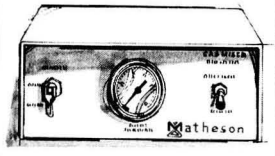

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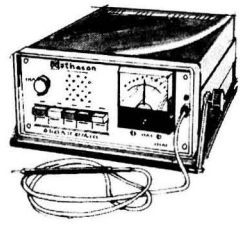

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INTERNATIONAL

About 50% of energy needs supplied by solar is Romania's goal. Scientists believe that the country could then save about 8 million tpy of fuel. In fact, solar is in use already to heat baths at the Black Sea resort of Saturn, for 1200 guests at 3 hotels; this is believed to be the largest such project in eastern Europe. It works 5 mo/y, and saves about 70% of fuel costs. Solar is also slated for agriculture, and various industries such as textile, food processing, and forest products. And the Energy Research Institute (Bucharest) is designing a solar electric plant. A "solar map" of the country is also in preparation.

WASHINGTON

President Carter's second environmental message calls for a 10-y program on acid rain, which results when atmospheric pollutants from the burning of fossil fuel are deposited by rain. Lead agencies in the acid rain program are the Department of Agriculture and the EPA; the program will have an interagency committee with representatives from another seven agencies. It is divided into five parts—monitoring, calibrated water sheds, a basic research program, interrelated long-range transport, and economics. Acid rain turns out to be the second presidential initiative in an environmental area; a first was former president Nixon's initiation of the RAPS program (*ES&T*, June 1978, p 644).

EPA's fiscal 1980 appropriation is $4.6 billion, of which $3.4 billion is designated for the sewage treatment construction grants program, and $1.2 billion for the operating budget. The agency's R&D budget was slashed by $6 million to about $234 million, but it is still 6.7% greater than fiscal 1979. Reductions in the agency's anticipatory research program and its toxic substances health and ecological effects research program were almost balanced by increases in its Great Lakes and integrated pest management research programs.

EPA is considering using the construction grant funds to cover projects other than water-pollution control. These so-called multiple-purpose projects could be designed to combine wastewater treatment with solid waste management—including hazardous waste disposal—or energy production, for instance. An agency position paper, "Strategies for Funding of Multiple-Purpose Projects," dated June 1979, enumerates the options but makes no recommendations. *ES&T* will discuss the options in an Outlook in an upcoming issue.

Rep. Bob Eckhardt

A sobering CEQ report on atmospheric CO_2 buildup may put a halt to or at least reduce the speed of passage of the spate of bills concerning the development of synthetic fuels now wending their way through Congress. Four environmental scientists, in their report to the Council on Environmental Quality, wrote that increased use of fossil fuels, and especially synfuels, will increase atmospheric carbon dioxide, leading to an increase in the earth's surface temperature; this warming could in turn lead to shifts in climatic zones and displacement of agriculture. The warming trend will "probably be conspicuous within the next twenty years." Rep. Bob Eckhardt (D, Tex.) called the synfuels program "a direct assault on the free enterprise system," that would add to the rate of inflation and reduce industrial productivity.

The EPA's current tally of potentially dangerous hazardous waste sites has reached 151 with the addition of another 60 newly discovered sites across the nation. According to deputy administrator Barbara Blum, the agency's "highest priority" is the cleanup of hazardous waste dump sites that threaten public health. To this end, the EPA has established an agency-wide hazardous waste enforcement and emergency response system to respond to emergencies. However, the agency is still "uncertain" of its ability to meet the court-mandated deadline (December 31 for Sections 3001–3004, and October 31 for Sections 3005–3006) for issuing the hazardous waste regulations called for under the Resource Conservation and Recovery Act.

The Dept. of Energy concludes that alcohol fuels can help the U.S. stretch its petroleum supplies through the 1980's. This rather belated conclusion can be found in "Report of the Alcohol Fuels Policy Review," DOE/PE-0012, prepared under the direction of the assistant secretary for policy and evaluation, Al Alm.

Pesticide matters. EPA has temporarily halted the remaining uses of DBCP, citing new evidence of potential health hazards to consumers, farm workers, and pesticide applicators. The U.S. producers of dibromochloropropane have, however, requested a hearing contesting the suspension order; during the hearing period, DBCP use will be permitted. The agency will permit growers of wheat, apples, and some cotton to continue to use the pesticide endrin. Restrictions, however, have been mandated; these include

protective clothing and precautions on product labels. And, finally, the EPA is considering a public hearing on the nonsuspended use of the herbicides 2,4,5-T and Silvex.

STATES

Georgia becomes the first state to withdraw from the federally funded coastal zone management program. In giving up the funds, about $500 000 annually, the state cited "frustration" and "continuous harassment" as reasons for this voluntary action. Georgia plans to manage its coastal resources through existing state programs, relying solely on the state revenues for funding. Georgia has been in the federal program 5 y, and has received more than $2 million in grants and $1.2 million in loans.

N.Y. DEC's Flacke

"New Yorkers will be footing the bill to clean up Ohio's dirty air," Environmental Conservation Commissioner Robert F. Flacke said concerning EPA's decision to relax clean air standards for two Cleveland power plants. The Dept. of Environmental Conservation has determined that much of the state's sulfate and fine particle pollution originates from combustion of fuels in the Ohio area. Flacke said that these contaminants have contributed to the acid rain problem in the Adirondacks. In a letter to EPA administrator Douglas Costle, Flacke called for a reevaluation of airshed boundaries "to make sure all states live up to the same clean air goals."

Portland, Oreg., is drafting comprehensive energy conservation rules, perhaps the most comprehensive in the U.S. According to the *New York Times,* proposed legislation calls for mandatory "weatherization" within 5 y of all privately owned buildings; energy audits for all homes and businesses; a special gasoline tax to finance traffic-flow improvements; and new zoning regulations to assure each home "solar rights," that is, access to solar exposure. Energy analysts claim that Portland's plan could save residents 30% of their current energy use by 1995, even if cheaper hydropower was not available to the city.

An environmental toxicology training program has been set up at Dartmouth Medical School, Hanover, N.H. The program, which began July 1, is funded by a National Institute of Environmental Health Sciences grant for $329 959. Four persons began predoctoral studies in the program, and a fifth person will soon begin postdoctoral work. The interdisciplinary program involves the medical school's departments of Pharmacology and Toxicology, Anatomy, Cytology, and Pathology, and Dartmouth College's Environmental Studies Program.

After a rather shaky development period, Baltimore's pyrolysis solid waste plant is now "working, and it's working well," Mayor William D. Schaefer says. The city made modifications to the plant abandoned by Monsanto Co. in February 1977, and serious air pollution problems are said to be corrected. Baltimore plans to operate the plant daily, six days a week. Six hundred tons of solid waste is fed into the plant daily, and the hot gases from the pyrolyzed refuse are used to produce 1.4 million lb of steam daily. The steam is purchased by the Baltimore Gas & Electric Co.

PCB watch. North Carolina was told by the EPA that it could not treat in place the 210 mi of PCB-contaminated highway. The state wanted to treat the highways with activated charcoal, but with the EPA denial it will now look for storage sites in each of the 14 counties in which PCBs were dumped. The cost of removing the PCBs from the highways to the dump sites is estimated at $2 million, plus the cost of storage. Pennsylvania's Dept. of Environmental Resources reports that fish in the Shenango River are not contaminated with high levels of PCBs, although sediment samples from the river taken below the outfalls of a Westinghouse Electric plant at Sharon contain relatively high levels of the chemical.

MONITORING

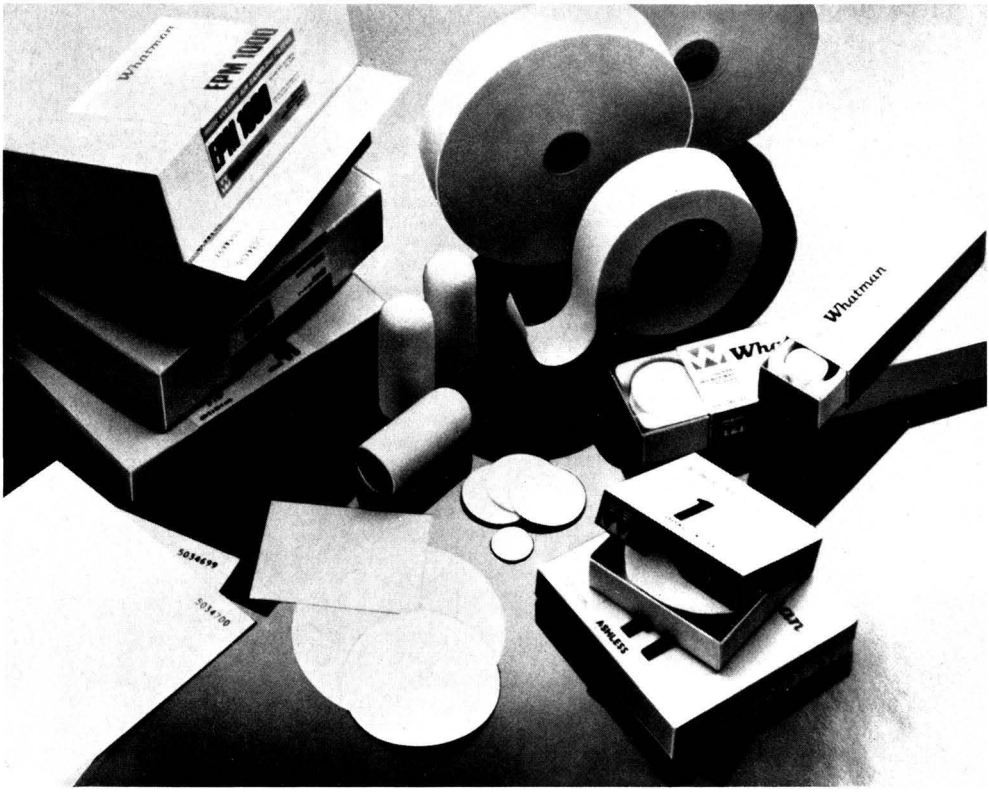
Sludge blankets can be watched by means of an advance in photometric measurement technology. What is used is the MEX_2 offered by Eur-Control USA Inc. (Decatur, Ga.). It measures solids concentration or turbidity as a function of optical characteristics, and uses a dip or sensing probe. The probe is unaffected by up to 90% obscuration, and is placed directly into the line, tank, or reservoir to be measured. When solids reach a turbidity level of 1000 ppm, a visual alarm is activated. Presently, the device is in use at Hoechst Chemical Co.

TECHNOLOGY

Improvement of rectangular filter performance for distributing wastewater is brought about by use of the Coanda effect, which is also the basis for fluid amplifiers. The Coanda effect involves the tendency of a fluid to cling to an adjacent surface, until moved away from that surface by some other force. For a rectangular filter, the result is improved, more efficient wastewater flow over the filter, in an enhanced trajectory, according to Paul Hyde of Neptune Microfloc, Inc. Flow assumes a "doughnut" pattern, rather than the normal "umbrella" pattern. The Coanda effect has been used to make modules, for other applications, that can perform certain computer logic functions.

Ammonia can be removed from wastewater and recovered for fertilizer making because of a new treatment process invented at Bethlehem Steel. The ammonia is distilled through two 90-ft stills, and is processed through associated equipment. It is taken from weak ammonia liquor (WAL), a byproduct of coke gas. The old method of countercurrent distillation of ammonia was kept, but a new design cut still size, steam needed, as well as steam pressure, and downtime. Fouling no longer occurs. Phenol, remaining in the liquor after ammonia removal, is easily biotreated, and converted to carbon dioxide and water.

Essentially passive solar energy will save 70% of energy costs in a new 2 million ft^2 office/service complex that the Tennessee Valley Authority (TVA) is building in Chattanooga, Tenn. It will use solar light,



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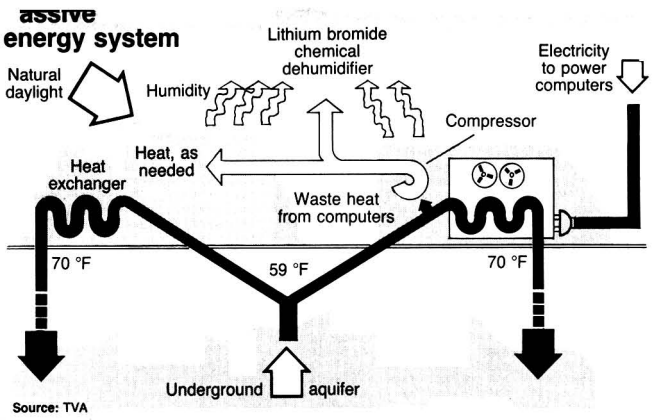

Source: TVA

groundwater cooling, computer-controlled waste heat, and chemical dehumidification principles. The complex will house more than 3000 employees. In corridors, sunlight will substitute for artificial lighting, for example. Waste heat will be supplemented by heat pumps. With an average temperature of 59 °F, the groundwater is an effective coolant. Building shaping will also maximize solar use and energy savings.

A "biomass energy machine" can produce energy equal to 432–1088 gph of diesel fuel, net after machine diesel consumption. Developed by Georgia-Pacific (Portland, Oreg.), it is presently usable in flat terrain, though other models, for more rugged land, should be developed in the future. The "fuel" would be otherwise useless brush that needs to be suppressed, anyhow, if pine trees for paper are to have more nutrients, water, and light. Nicknamed "Jaws 3," the machine chips brush to render it suitable for combustion. The brush would be harvested from each acre every 3 y.

Scrub SO_2 from high-sulfur coal, and get marketable sulfur. That is the purpose of the aqueous carbonate scrubber process developed by Rockwell International, and being tested out by Niagara Mohawk Power Corp., and others, in New York, through the nonprofit Empire State Electric Energy Research Corp. (ESEERCO). Not only would sulfur be extracted, but no significant waste disposal measures should be required. The concept will be demonstrated on a 25-y-old 100-MW unit at the Huntley Steam Station, along the Niagara River, at Tonawanda, N.Y.

Superheating methane and carbon dioxide (CO_2) might convert solar energy into usable electric power, according to the U.S. Naval Research Laboratory. A solar furnace heats to 1700 °F, so the gases form steam, as well as latent heat that can be stored. Another approach, developed at Clemson University, uses solar energy to produce hydrogen and a halogen from a hydrohalide, and could eventually recover the energy by recombination of the hydrogen and the halogen. The Clemson approach also uses cheaper, easier to make silicon cells, each the size of a "BB" pellet.

A new "tokamak" is helping scientists enhance fusion reactor development. It is located at Argonne National Laboratory (Ill.), and is one of the world's smallest—about 4.5 ft from one side of the "doughnut" to the other. Various experiments in extending "tokamak" life and enhancing plasma production will be performed.

INDUSTRY

"We need to retain and expand our environmental achievements while we seek energy alternatives." That is what the Environmental Industry Council (EIC, Washington, D.C.) heard from Rep. Joseph Fisher (D, Va.). He told the EIC to remain ready to make the necessary equipment, and to be on guard against attempts to weaken the various environmental laws and regulations presently in force, or to come. He said the EIC might profit from an energy trust fund, some of whose dollars may go to purchase anti-pollution equipment.

EPA's funding policy is "misguided" when it comes to alternatives to conventional gravity sewer systems, and creates numerous delays. It would also increase costs, according to a report that Energy and Environmental Analysis, Inc. (Washington, D.C.) prepared for the National Utility Contractors Association, Inc. (NUCA). The report for NUCA says that for communities of over 1500, gravity sewers and centralized treatment are more cost-effective than *any* on-site systems. For smaller populations, septic tank/soil absorption systems are more cost-effective, but must be properly sited. The report also said that alternatives were useful "for only 1.1–3.3% of the population."

The "Superfund" for old chemical dump sites—what should it address? Only "orphan" dump sites, the Chemical Manufacturers Association (CMA, Washington, D.C.) suggests. Such funding should be furnished through the regular federal budget process, and not by a tax on a single (chemical) industry, the CMA says. Also, states should participate in funding, and establish problem site priorities. Moreover, the CMA recommends that the fund be used for emergencies based on these priorities, and that wrongful dumpers should be made to contribute to the fund, with liability based on comparative responsibility.


R-C's Walker

The largest contract for fabric filters ever awarded for a single boiler, valued at about $15 million, went to Research-Cottrell, Inc. (R-C, Bound Brook, N.J.), for design, materials, and construction. Alan Walker, R-C's vice president and general manager for the Utility Division, explained that a special acid-resistant polymer finish will protect the nearly 13 000 bags from fiber abrasion and wear. The system will be supplied, on a flange-to-flange basis, for a 550-MW boiler at Houston Lighting & Power Co.'s Parish Station, Unit No. 8, and will have a reverse-air cleaning system. Walker predicted a 1982 completion, and 1983 start up.

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.0020	— Sample No. 5 Absorb.
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40.	— Sample No. 4
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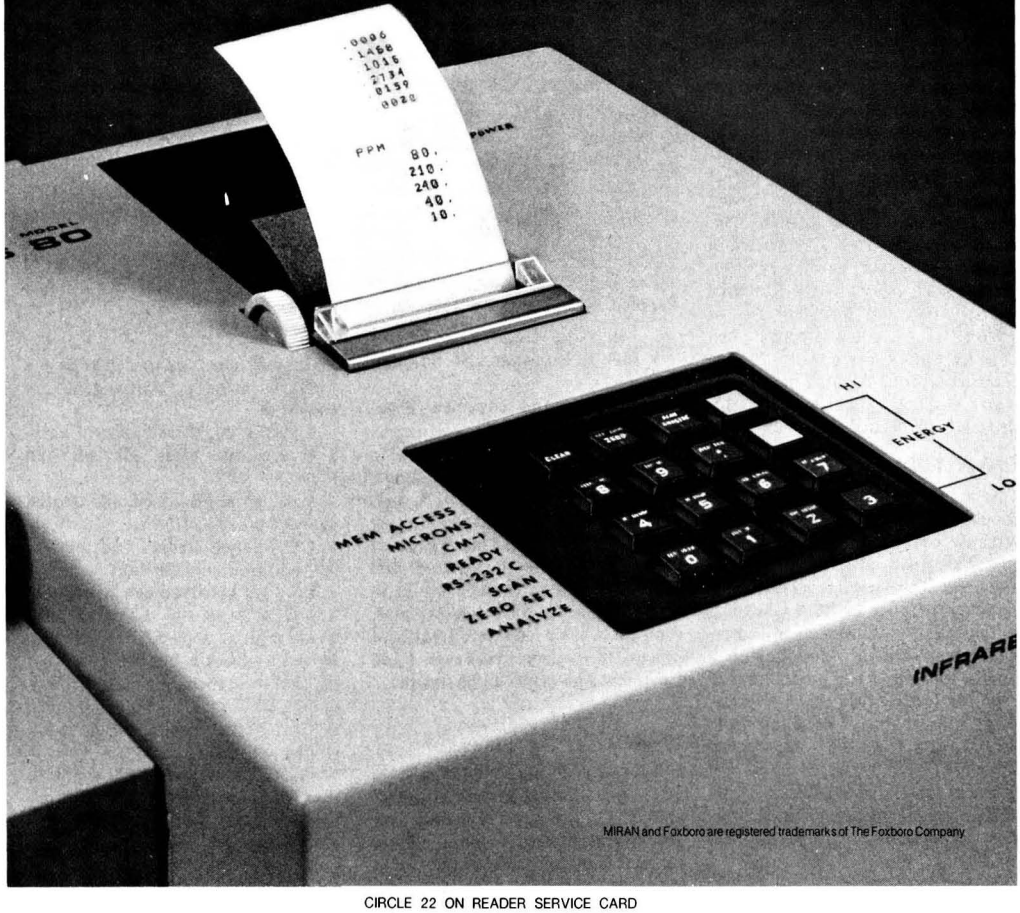

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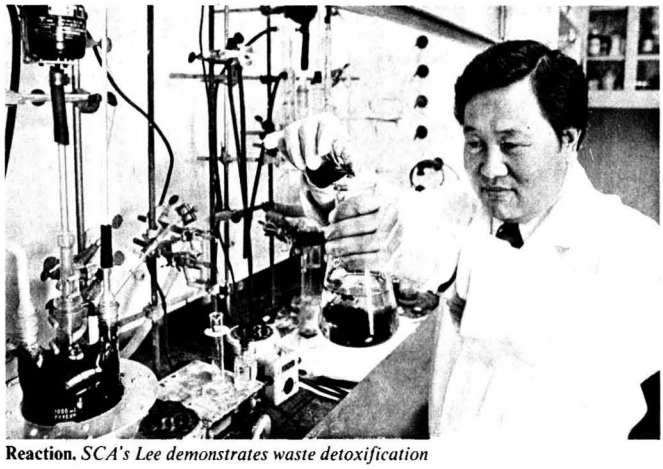
CIRCLE 22 ON READER SERVICE CARD

Hazardous wastes- can they be reused?

A division of SCA Chemical Waste Services, Inc., says "yes," and has several approaches to accomplishing this recycling objective

"One company's waste is another company's resource." How often have you heard that said as an analogy to Aesop's, "One man's meat is another man's poison"? However, there may be some truth to the first quotation, if one takes into account the fact that the waste must usually be processed in certain ways, before it can be transformed into a resource. Such transformation is especially necessary if the original waste is hazardous.

Until now, most hazardous and other waste disposal was done according to the "out of sight, out of mind" method. Wastes were tossed into the ocean, abandoned on land, injected into deep wells, or buried in landfills. However, various environmental laws, especially the Resource Conservation and Recovery Act of 1976 (RCRA), would effectively ban or at least place severe restrictions on these older, time-honored methods of waste disposal. Clearly, other approaches are needed.



Reaction. *SCA's Lee demonstrates waste detoxification*

Groups of wastes

One approach involves a new philosophical view that all incoming waste streams could be regarded as raw materials that contain recoverable resources. This view has been reduced to actual practice by SCA Chemical Services Co., a Division of SCA Services, Inc. (Boston, Mass.), with a unique waste-to-waste processing and recovery facility located in Newark, N.J., and capable of handling up to 500 000 gpd. Incoming waste streams are classified as major chemical and physical functional groups, based on certain unique operations, such as:

- organically contained aqueous waste
- acid recovery
- fuel reclamation and formulation
- acid/base and redox neutralization
- hazardous waste detoxification.

To be sure, these process classifications are interrelated, as S. K. Lee, Director of Research and Engineering at SCA, pointed out. That is because secondary or waste products of one process can often become useful in another process. Also, Lee explains, each class has a "discrete treatment process of its own." However, these treatment processes can be flexible.

Products

The aim of SCA's approach to waste treatment is to help chemical companies solve waste problems in an economical manner, and to obtain useful chemical products or fuels, or at least harmless residues, simultaneously. Products generated at SCA's Newark recovery facility generally consist of:

- recovered, marketable, or reusable organics, acids, alkalies, and fuels
- chemical detoxified, and treated aqueous process effluent
- dewatered sludges and inactive concentrated solid residues.

Recovered products can be stored in a tank farm, on-site. The tank farm would meet all applicable regulations. However, SCA's Lee believes that many of these reclaimed materials will, in fact, prove to be highly marketable, so that "actual on-site storage needs will be minimal."

Treated aqueous effluent is passed through automatic sampling/monitoring stations. Then it is discharged according to permit terms, to the Passaic Valley Sewer System. In addition, sludge and solid residue are prefixed

for disposal at a "scientifically" secured landfill that SCA operates. "Scientifically secured" means that all waste in the fill is chemically classified and catalogued according to operating permits. If the waste is ever needed as a resource, it can thus be retrieved at some future time.

Suppose that an industrial client inquires about disposal of a specific waste material arising from a given manufacturing process. SCA obtains all pertinent information, as well as waste samples. The samples undergo physical and chemical analysis at Newark. Then, treatment or recovery processes can be devised. A specific system is put into operation, as well as a transportation schedule. If, however, the contents of the waste transported to SCA are at variance with those found in the original chemical analysis, the client is so informed, and the change is resolved.

An alternative treatment or recovery mode is set up through a complete systems analysis to determine what must be neutralized or detoxified, what can be recovered, and how to go about these tasks. Afterwards, necessary process modifications are made, in order to achieve waste treatment or beneficiation goals. But before this is done, a stringent technical/economic analysis, with a pilot facility, is performed.

Monitoring

At SCA's Newark facility, waste materials and products are continuously monitored by means of up-to-date analytical instrumentation. Systematic sampling begins when the waste is transported from the client's plant, and ends when it has been transformed into a marketable product that is sold, or an innocuous substance that has been properly treated for disposal. The idea, SCA says, is to assure the customer that the problem of hazardous (or nonhazardous) waste disposal is solved, as soon as the waste leaves the customer's plant. That becomes especially important now, because in New Jersey, for instance, the producer of a waste is responsible for its ultimate disposal, and RCRA will make a hazardous waste generator answerable not only for proper disposal, but even for safe transportation.

A common denominator

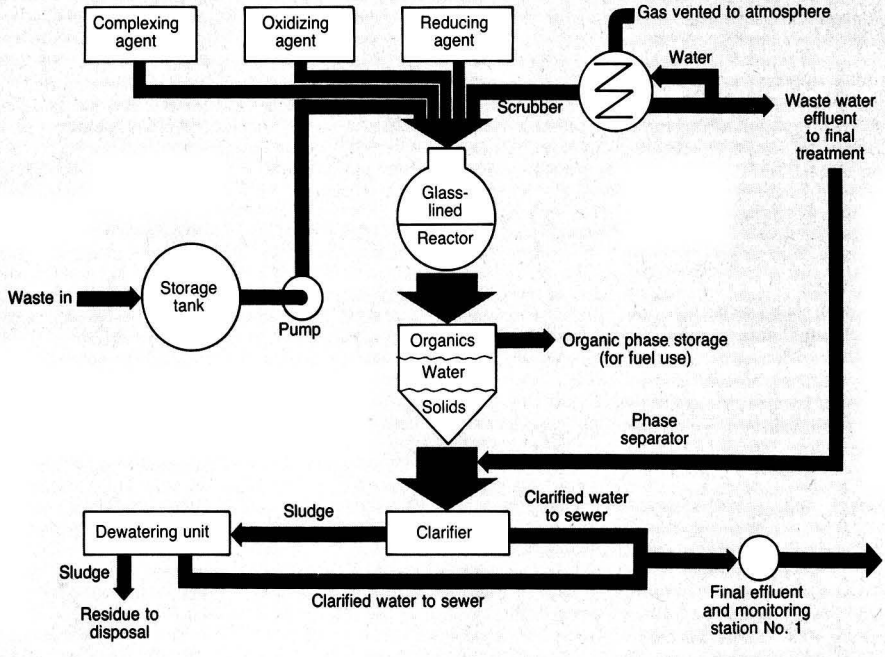
Probably other companies will enter the hazardous waste treatment/beneficiation field. For example, Rollins Environmental Services (Wilmington, Del.) has applied for EPA clearance to incinerate at high temperature, thus rendering harmless PCB-containing sludges, at a facility in Southern New Jersey (*ES&T*, July 1979, p 780). No doubt, others will follow, handling different wastes by a variety of methods. Most likely, however, the common denominator is this: that private enterprise is embarking on new paths to find imaginative, yet reliable ways to comply with forthcoming RCRA regulations concerning hazardous wastes. JJ

Hazardous waste detoxification

Treating hazardous wastes

Wastes vary; therefore, the treatment operation cannot be standardized. But, depending upon what the wastes are, chemical, catalytic, complexing, and oxidation-reduction techniques are available. Optimum approaches are determined after careful systems analyses.

If any pollutant gases are generated through a waste treatment process, such gases are removed by "scrubbing" and absorption. The "scrubbed" waste is discharged after final treatment. Here is a representative detoxification process.



A warming of solar energy

A first 1-MW plant, mini OTEC, is operating off Hawaii

Ocean thermal energy conversion (OTEC), the process of using the warm surface water of the tropical ocean and the cool water from a half-mile below to produce energy, is making progress. Much has been achieved, it was learned at the recent 6th annual OTEC meeting (Washington, D.C.), since the 5th last year in Miami. Achievements to date are in the areas of component testing, biofouling testing, and heat exchanger evaluation.

Sponsored in large part by industry, the mini OTEC-1 is an attempt to put the process on a sound technical base. This first ocean-based plant was commissioned off Hawaii on May 29, 1979. Test data from this platform are expected by May 1980. So, within the next year, OTEC will be demonstrated. Within the next one to one and one-half years it is expected that a major upward shift in gears will occur in this solar technology area.

Hurdles

There are, however, several concerns. The OTEC credibility problem has been facing us for years. First, some people, for example, become uncertain that the 40 °F temperature difference will run the heat engine. During their schooling, engineers learned that the larger the temperature difference the more work one can get out of a system.

A second problem centers on the product from the OTEC plant. OTEC either produces electricity or an electric energy intensive product such as aluminum or ammonia. Electricity is not a dominant concern facing the U.S. today; now the problem is a liquid fuels problem. While it is true that the national growth for electricity has slowed, it seems certain that OTEC is going to be used in certain areas over the next 15–20 years.

Electricity can be produced by different ways today—burning coal, oil, and natural gas. In order for OTEC to enter this field as an alternative energy source, it is necessary to find the market for this solar energy option.

OTEC, at a glance

Its potential. OTEC can produce, at competitive cost, 90 trillion kWh of power, 40 times the electric power used in the U.S. last year.

It's renewable. The sun continuously renews the warm surface water. Hence, ocean thermal energy is a renewable energy source. We don't have to pay someone for it. Under international law, its use is free.

One plan to get OTEC on line is slowly emerging, at least in concept. Island dependencies, not only of the U.S. but of other global neighbors, rely totally on imported energy—home fuel oil, car gasoline, jet fuel, and boat residual oil. All of the island economies are dependent on imported fuel. In terms of this scenario, the visibility of the OTEC will be enhanced by making U.S. island economies independent of imported oil. Then, OTEC might be used as a springboard for entry in the U.S. in the 1990's.

Another concern is engineering choices. OTEC is proven technology; it's all economics, as reported earlier (*ES&T*, July 1977, p 651). What makes the design choices so difficult is that by now there are six different materials for the heat exchangers, eight different heat exchanger designs, six or seven different pipes, and six platforms that have been advanced for the design of the system. These choices present some 1500–1800 different types of OTEC's that can be built.

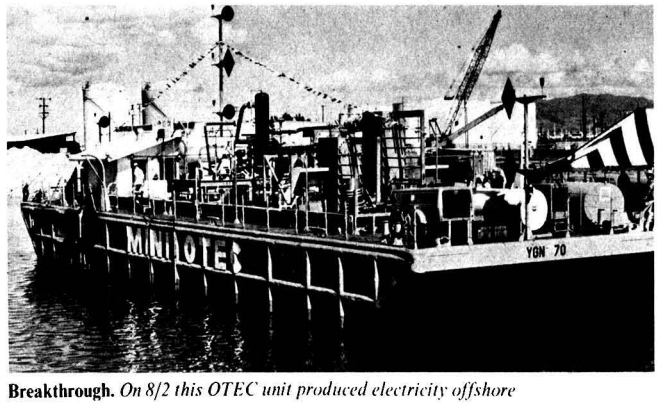
OTEC goes global

The ocean gradient is a renewable, international resource in search of financial support. A prevailing mood from the Law of the Sea Conference is to extend a nation's jurisdiction to the 200-mi limit. For these reasons, France and Japan are interested in OTEC and are making progress on their own.

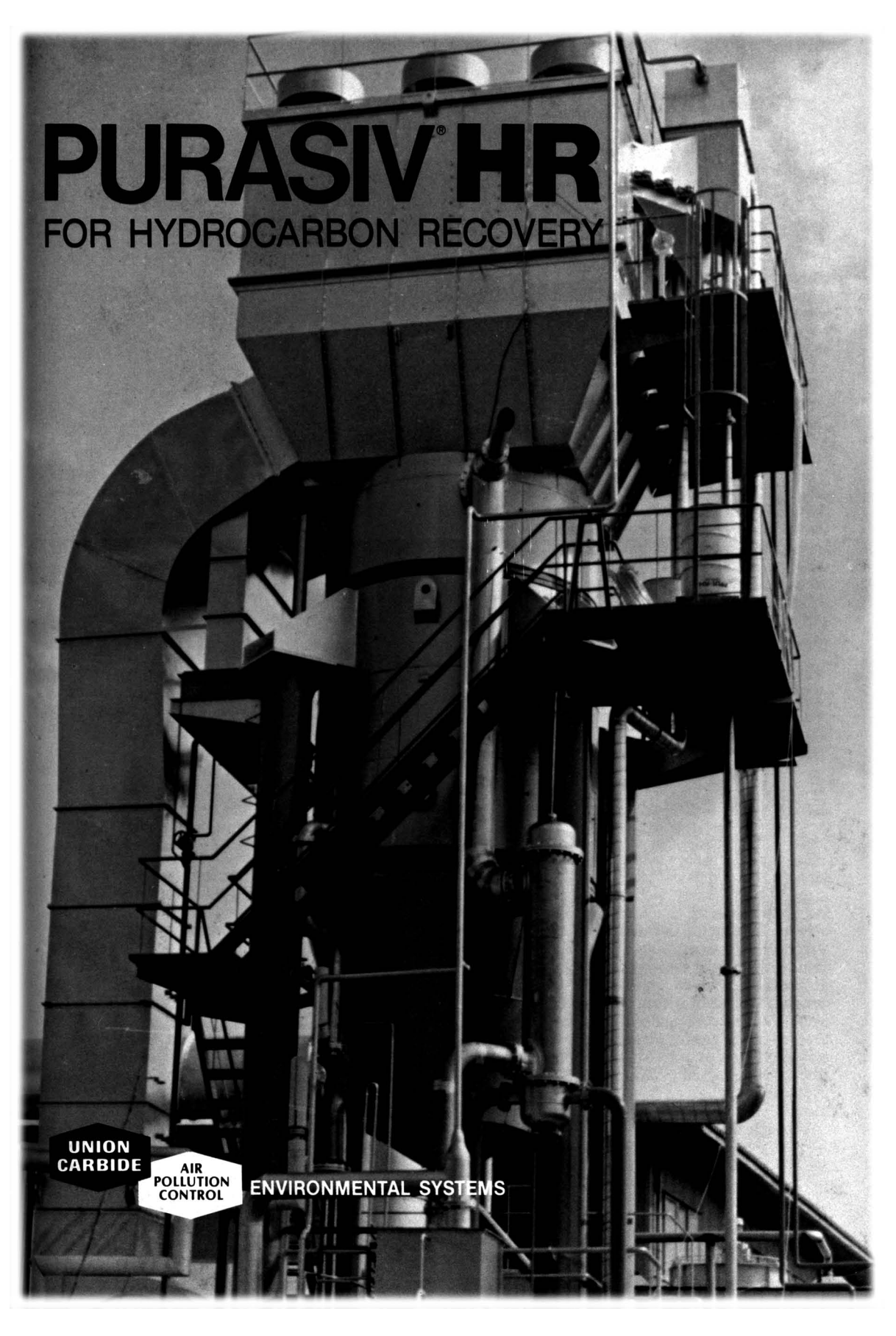
K. Kamogawa of the Tokyo Shibaura Electric Co. (Kawasaki) said that the Japanese started their OTEC activity in 1970. For obvious reasons, including small land mass, an adequate thermal gradient area, and a large water resource to the 200-mi limit, Japan started their activity. Kamogawa mentioned that they were using titanium heat exchangers.

P. Marchand said that France is interested in OTEC because it looks attractive, it's a French idea from D'Arsonval in 1881, and within its 200-mi zone France has a number of islands that are fuel dependent. The government agency, CNEXO (Paris), is in charge of the French program.

An industrial OTEC group got started in 1978. Terming it EUROCEAN, B. Lachmann said that this project is headquartered in Monaco and represents the interest of nine companies including four in Sweden, two in Italy, and one in Holland. EUROCEAN is planning a 10-MW (megawatt) plant; another EUROCEAN activity is a combination of OTEC with aquaculture; here, a number of countries are interested in the concept. SSM



Breakthrough. *On 8/2 this OTEC unit produced electricity offshore*


PURASIV® HR
FOR HYDROCARBON RECOVERY
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AIR POLLUTION CONTROL
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The PURASIV® HR System

The PURASIV HR System exclusively marketed in the U.S. and Canada by Union Carbide Corporation* represents advanced, second generation technology for the removal and recovery of hydrocarbon vapors from air by activated carbon adsorption. It is a continuous fluidized bed adsorption system operating with separate sections for the adsorption and desorption steps.

The key to the PURASIV HR System is the unique adsorbent employed—a spherical, beaded activated carbon that possesses two physical characteristics essential for continuous fluidized bed operation:

- Uniform spherical shape that provides a homogeneous fluidized bed in the adsorption section and remains free-flowing in the dense bed desorption section of the process.
- Resistance to attrition for long service life and trouble-free operation.

The spherical beads of activated carbon are produced by a proprietary process developed by Kureha Chemical of Japan. Molten petroleum pitch is shaped into spherical particles and subsequently carbonized and activated under closely controlled conditions to yield activated carbon beads suitable for vapor phase adsorption.

Figure 1 is a photograph of the beaded activated carbon along with a sample of 4 x 6 mesh conventional pelletized activated carbon.

*PURASIV is a trademark of Union Carbide Corporation which markets the PURASIV HR System under an exclusive license from Kureha Chemical, Japan.

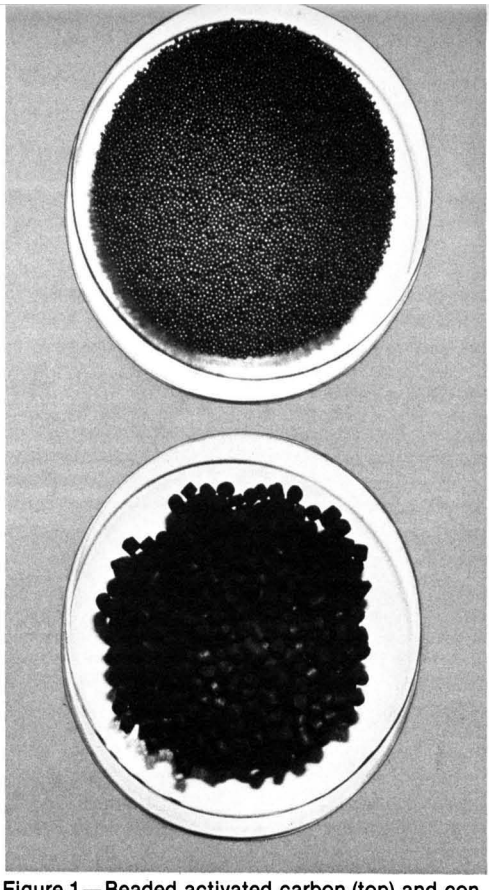


Figure 1—Beaded activated carbon (top) and conventional pelletized activated carbon.

Activated Carbon Adsorption

The basic technology employing carbon adsorption for solvent recovery was pioneered by Union Carbide in the 1930's. The basic technique is a two-stage, fixed bed operation in which the adsorbent beds alternate between adsorption and desorption cycles. Solvent laden air is passed through a freshly regenerated static bed until the adsorbent loading reaches a predetermined level or until solvent breakthrough occurs. The feed air is then switched to a second bed while the first bed undergoes regeneration. Low pressure steam passing through the loaded adsorbent serves the dual purpose of raising the bed temperature and reducing the partial pressure of the adsorbed hydrocarbons, allowing them to be released in vapor form.

Although the advantages of continuous operation were well known, conventional forms of activated carbon previously available were subject to severe attrition losses under the conditions required for fluidized bed operation. With the development of the spherical beaded adsorbent used in the PURASIV HR System, the following operating advantages have been realized:

- Countercurrent flow of solvent laden air through the fluidized adsorbent assures maximum utilization of adsorption capacity.
- High superficial velocity achieved in the fluidized bed overcomes problems of poor gas distribution often encountered in the fixed bed process. Uniform gas distribution eliminates localized hot spots and the bed fires that have plagued fixed bed units handling highly reactive solvents, such as ketones.

Continuous Solvent Removal/Recovery

As shown by the PURASIV HR System reactor drawing (Figure 2), solvent removal from effluent air and its subsequent recovery in the desorption section is a relatively simple, straightforward operation. Solvent laden air is introduced into the bottom of the adsorption section and passes upward countercurrent to the fluidized activated carbon in a series of patented trays. Adsorbent on each tray is totally fluidized, flowing downward from tray to tray by overflowing a weir/downcomer arrangement.

As it leaves the bottom tray of the adsorption section, the activated carbon is no longer fluidized and flows as a dense bed through the desorption section of the column. The adsorbent first passes through the tube side of a shell-and-tube heat exchanger where indirect heating by steam or other suitable heat transfer media raises it to the desorption temperature. The steam used for indirect heating is condensed and returned uncontaminated as condensate return to the boiler.

Solvent is then desorbed from the activated carbon by the introduction of direct contact steam. This steam (stripping gas) is introduced at the bottom of the heat exchanger and flows countercurrent to the adsorbent in the tubes. The direct contact steam (stripping gas) reduces the partial pressure of the hydrocarbons and sweeps them from the bed in vapor form.

The stripping steam, together with the desorbed solvent, is removed from the column and the mixture is condensed for separation and recovery of the solvent. The activated carbon leaving the bottom of the desorption section flows to an air lift where it is air-conveyed to the top tray of the adsorption section.

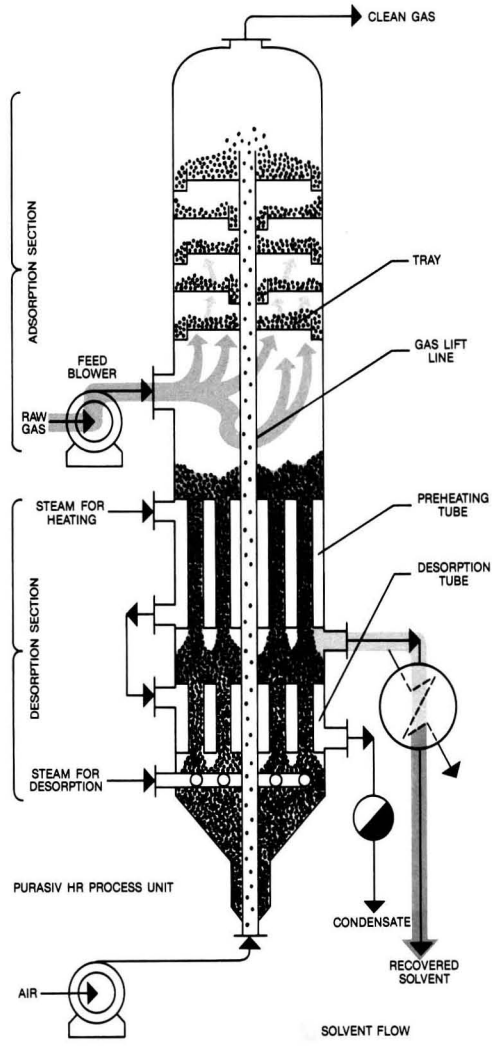


Figure 2—PURASIV® HR Flow Diagram
Steam Stripping

Solvent Stripping Modification

The basic PURASIV HR System described above is used for removal and recovery of chlorinated hydrocarbons and other water insoluble hydrocarbons. It is designated as Type S to denote that steam is utilized for the stripping gas.

For operations where steam stripping is not desirable, an optional flow scheme—Type N, shown in Figure 3—is designed to use nitrogen as the stripping gas. In this version of the PURASIV HR System, the adsorption section is unchanged. However, a secondary adsorber must be added ahead of the desorption section in order to properly condition the recycle nitrogen stream. This is necessary because the nitrogen vented from the solvent separator is saturated with hydrocarbons. Direct recycle of this saturated nitrogen would increase the concentration of undesorbed hydrocarbons. This would, in turn, increase effluent concentrations when the adsorbent is returned to the top adsorption tray.

The nitrogen stripping technique affords unique advantages when removing and recovering water soluble hydrocarbons. The process introduces no water contamination of the recovered solvents, except for the moisture present in the solvent laden air. Provided the relative humidity of the incoming air is less than 60%, solvents recovered by the Type N System will, in most cases, contain less than 5% water by weight.

The Type N System also offers the advantage of reducing operating costs by using recycled nitrogen as the stripping gas instead of using steam on a once-through basis. Capital cost of the N version is somewhat higher, because the secondary adsorber is required for conditioning the recycled nitrogen.

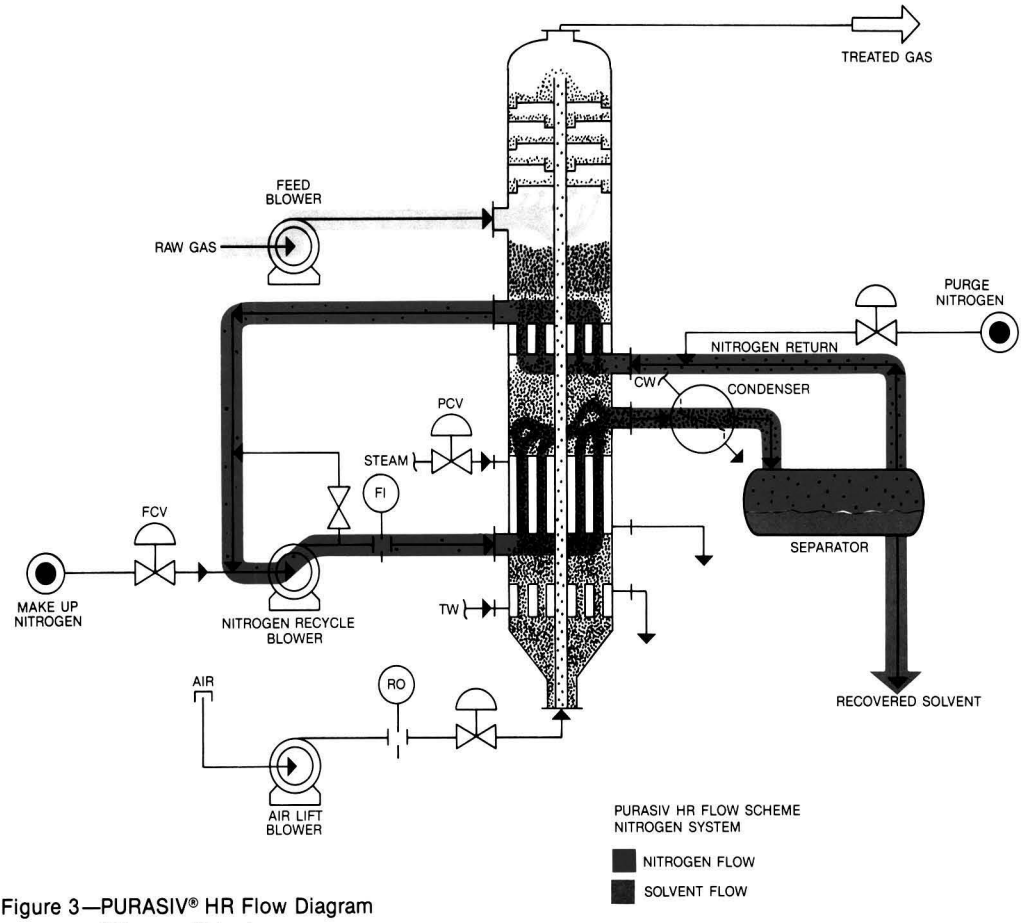


Figure 3—PURASIV® HR Flow Diagram
Nitrogen Stripping

Proven Process Applications

There are now over forty commercial plants in operation in Japan. A partial list of these commercial installations is shown in Table 1. Adaptability of the PURASIV HR System is indicated by the types of solvents, range of flow rates, and influent/effluent concentrations achieved in actual applications. Table 2 presents similar data on the first three commercial installations in the U.S.

Table 3 presents operating data for three commercial units.

TABLE 1 • COMMERCIAL EXPERIENCE

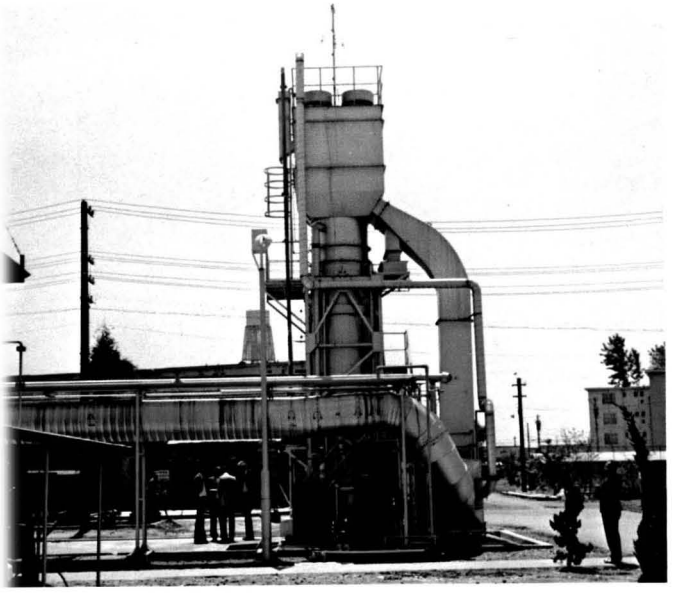
Industry	Flow Rate (cfm)	Type of Solvent	Concentration In (ppm)	Out (max)
1) CLOTH WASHING	700	CHLORINATED SOLVENT	3,500	100
2) DEGREASING	1,000	CHLORINATED SOLVENT	3,500	50
3) CHEM. PLANT	1,800	CHLORINATED SOLVENT	3,560	100
4) CHEM. PLANT	400	CHLORINATED SOLVENT	5,000	10
5) CHEM. PLANT	400	CHLORINATED SOLVENT	500	10
6) FILM COATING	8,500	AROMATIC SOLVENT	2,680	80
7) SURFACE COATING	4,200	THINNER	100	—
8) DEGREASING	700	CHLORINATED SOLVENT	1,000	50
9) DEGREASING	900	CHLORINATED SOLVENT	1,500	50
10) DEGREASING	900	CHLORINATED SOLVENT	1,500	50
11) DEGREASING	1,000	CHLORINATED SOLVENT	3,500	50
12) DRY CLEANING	200	CHLORINATED SOLVENT	10,000	50
13) PRINTING	6,000	AROMATIC SOLVENT	1,800	50
14) PRINTING	1,400	MIXTURE	1,450	50
15) DEGREASING	1,400	CHLORINATED SOLVENT	600	50
16) DEGREASING	2,100	CHLORINATED SOLVENT	600	50
17) DEGREASING	1,400	MIXTURE	390	40
18) ADHESIVE	29,000	AROMATIC SOLVENT	2,710	50
19) CHEM. PLANT	1,000	ALCOHOL	1,200	50
20) AUTOMOTIVE	140,000	ODOR REMOVAL	20	.4
21) NYLON PLANT	8,400	CYCLOHEXANE	2,100	100
22) LAMINATOR	4,200	TOLUENE ETHYLACETATE, HEXANE	2,000	50
23) DEGREASING	11,750	CHLORINATED SOLVENT	1,500	50

TABLE 2 • COMMERCIAL PURASIV® HR SYSTEMS INSTALLED IN U.S.

Application	Air Flow, cfm	Solvent	Inlet Conc., ppm	Effluent Conc., ppm	Start-Up Date
Gravure Printing	78,000	Toluene	1,500	<50	1979
Automotive Top Coat Spray	6,000	Mixture	500	<50	1979
Photographic Film Coating	6,000	Ketone	8,000	<80	1979

TABLE 3 • COMMERCIAL SYSTEMS OPERATING IN JAPAN

	Unit I	Unit II	Unit III
Air Flow, scfm	6,000	8,000	29,000
Solvent Type	Toluene	Toluene	Toluene
Influent Conc., ppm	1,800	1,700	2,700
Effluent Conc., ppm	80	30	50
Solvent Recovered, lbs/hr	200	225	1,200
Electrical Usage, kw	20	22	120
Steam Usage, lbs/hr	200	220	1,800
Nitrogen Usage, scfh	13	17	—



This 8,000 scfm unit at a film processing plant has been recovering about 225 lbs/hr of toluene since 1975. Foundation is 20′ x 20′, height is about 35′.

The unit pictured at right has been in operation since 1976, handling 6,000 scfm of exhaust air from a gravure printing operation and recovering about 200 lbs/hr of toluene and xylene. The unit is installed on a 15′ x 15′ foundation and is about 30′ high.

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- Lower energy requirements—PURASIV HR Process requires only about 25 to 30 percent of the total energy required for a conventional fixed bed process.
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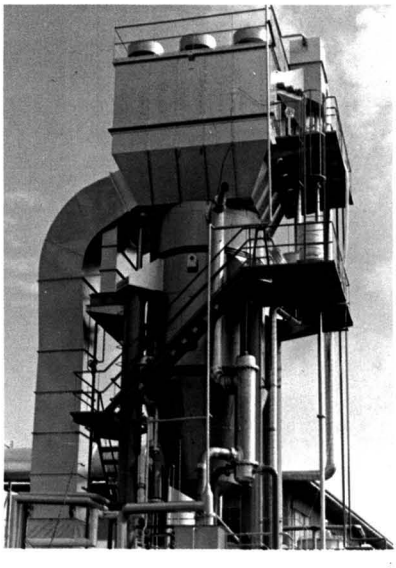
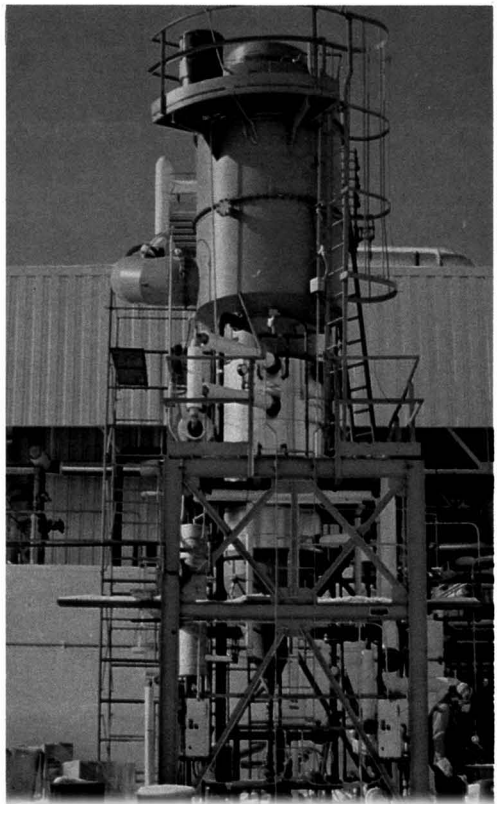
- Mechanically simple—PURASIV HR System requires no moving parts other than the incoming gas blower, desorption gas blower and adsorbent air lift blower. Cycling valves, control circuitry and instrumentation required for the fixed bed system are eliminated, resulting in:
  - •• High on-stream factors.
  - •• Greatly reduced maintenance costs.
- Compact size—PURASIV HR System unit requires relatively little land space, thus permitting advantageous location of solvent recovery equipment convenient to solvent storage or source of solvent emissions, reducing costs of ductwork for solvent laden air, and minimizing utility requirements.



An adhesive tape manufacturing plant has employed this 29,000 scfm unit since 1976, recovering about 1,200 lbs/hr of toluene. The unit is installed on a 30′ x 30′ foundation and is about 50′ high.



The 6,000 scfm unit pictured at right is recovering a mixture of solvents from an automotive top coat spraying operation. The unit was installed in early 1979.

...สมุด กรมวิทยาศาสตร์บริการ

Pictured left is the 70,000 scfm PURASIV HR System recovering 2,000 lbs./hour of gravure publication printing solvents. The system is installed in the United States and went on stream in 1979.

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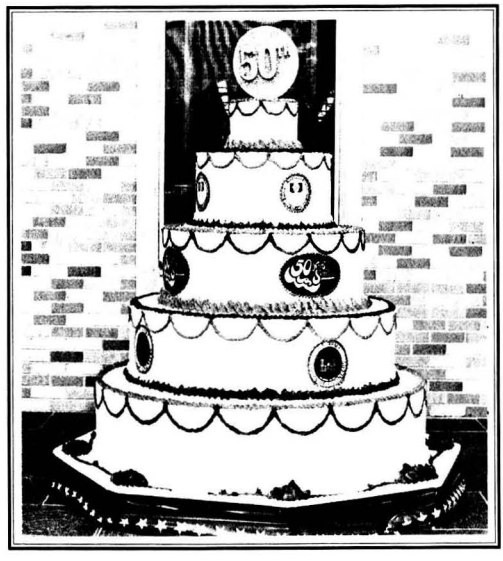
Happy birthday, WES!

On its 50th anniversary, the Army Waterways Experiment Station has a number of environmental missions to carry out. Here are some.



On June 23, 1979, the U.S. Army Engineer Waterways Experiment Station (WES) celebrated its 50th anniversary. Since its founding, the WES, located at Vicksburg, Miss., has grown to cover 685 acres. It now has 1400 employees, and a budget, this fiscal year, of $60 million. An increasing proportion of this budget is going toward projects related to environmental concerns.

Stabilizing sludges

Several of the tasks now under the purview of the WES Environmental Laboratory involve the effects of toxic materials released from hazardous wastes on local soils, and in water. Some of the ongoing hazardous waste disposal projects are sponsored by the EPA's Municipal Environmental Research Laboratory (Cincinnati, Ohio), and are directly related to regulations promulgated under the Resource Conservation and Recovery Act of 1976 (RCRA), and the Army's own pollution abatement program.

Norman Francingues, chief of the Water Supply and Waste Treatment Group of WES, told *ES&T* that one major study underway in his group is aimed at seeing if certain dangerous industrial sludges can be treated to render them insoluble and inert. The group is evaluating commercially marketed treatment processes for solidifying and chemically stabilizing industrial wastes. Treatment processes applicable to wastes such as those from electroplating, chlorine production, calcium fluoride, and flue gas cleaning sludges are included in this program. Several reports detailing results, and indicating applications of these techniques, are in preparation.

Another significant phase of research in Francingues' charge relates to the disposal or destruction of hazardous organic wastes. Efforts concerning organics are primarily part of the Army's mission, and not directly related to the EPA projects. The Army disposal operations are an outgrowth of programs related to pollution control at arsenals, and the destruction of obsolete or overaged weapons. For such "in-house" Army efforts, the group works with the U.S. Army Toxic and Hazardous Materials Agency, located at Aberdeen Proving Ground, Md.

Field investigations

Francingues and his group have conducted a number of field investigations to determine the pollution potential of different types of wastes in various geologic settings. However, access to some sites was difficult to obtain, and, in most cases, was restricted to a single visit, in order to take samples. Nevertheless, reports detailing site surveys have been prepared for municipal landfills, and for flue gas desulfurization sludge disposal sites. Also, a complete report addressing disposal sites containing treated industrial wastes is in preparation.

With respect to approved industrial waste disposal sites, Francingues predicted that these would be more diffi-

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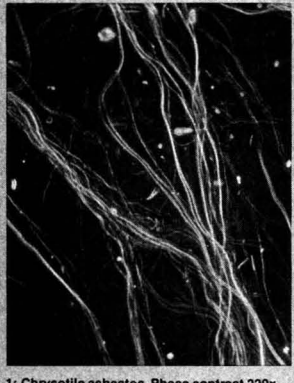
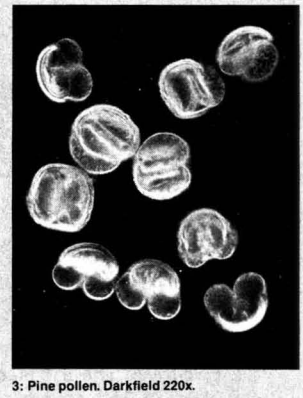
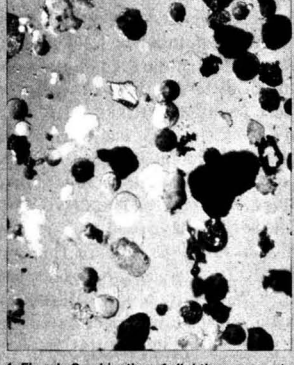


1: Chrysotile asbestos. Phase contrast 220x.

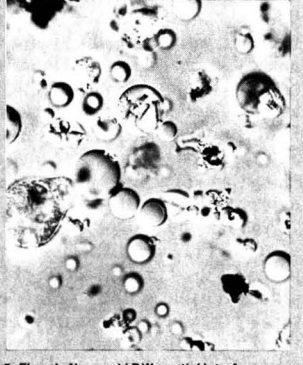
2: Chrysotile asbestos. Electron micrograph 9,500x.



3: Pine pollen. Darkfield 220x.



4: Fly ash. Combination of slightly uncrossed polarizers and reflected light 35x.



5: Fly ash. Nomarski Differential Interference Contrast 620x.

6: Detergent residue. Fluorescence 90x.

Photos 1, 2, 3, 4, and 6 by John G. Delly, Senior Research Microscopist, McCrone Research Institute.
Photo 5 by Dr. Robert F. Smith, Director of Biomedical Communications, New York State College of Veterinary Medicine, Cornell University.

cult to establish, if regulations under RCRA, as presently proposed, are finalized. *ES&T* asked about possibilities of retrofitting unsatisfactory sites, so that they may comply with RCRA requirements. WES research geologist Phil Malone answered, "How, for instance, would you install a 10-ft thick impermeable clay liner under an existing, operating landfill?" He and

Norman Francingues
evaluating hazardous waste methods

Francingues discussed the idea that impermeable, solidified sludge might be used in place of a clay liner under a waste landfill. However, they concluded that a great deal more testing and development would be needed before this approach could be considered as being proven.

Bioavailability of toxics

The Dredged Material Research Program (DMRP, *ES&T*, April 1976, p 327) was successfully completed in March 1978. Work is now being directed toward applying lessons learned from the DMRP, and formulating dredged material disposal guidelines that are technically sound. Also, in the future, these guidelines under the Clean Water Act of 1977 may be influenced by provisions of the Toxic Substances Control Act (TSCA) and RCRA, as well, WES scientist Richard Peddicord told *ES&T*.

Richard Peddicord
a bioavailability study

Simulation. *A miniature wetland*

With respect to toxic and hazardous pollutants in estuarine, marine, and wetlands areas, the focus of concern may be shifting from mere chemical presence to actual bioavailability, Peddicord said. However, it might be, he noted, that the environmental effects of such pollutants present could be mitigated by sorption on sediments, or reactions with naturally occurring materials, for example.

Peddicord explained that data indicate that contaminants dissolved in interstitial water, or otherwise loosely associated with sediment particles, may be elutriated. They can then be measured in samples of elutriating water by appropriate analytical methods.

Such contaminants may, in some cases, be bioavailable, and could then, conceivably, accumulate in the food chain. Bioassays could determine whether that is or is not occurring. On the other hand, if a contaminant becomes tightly bound to or incorporated in the sediment, it may not be elutriated, and, thus, would not be bioavailable.

What is a wetland?

As mentioned earlier, the DMRP has been completed. Yet, in a way, dredged material research of some kind must continue, since the Army Corps of Engineers retains responsibility for dredged materials, wetlands, and the like. "The National Environmental Policy Act and the Clean Water Act require continued input from the Corps in these areas," Bo Smith of WES' Environmental Resources Division reminded *ES&T*.

But just what *is* a wetland? Answers to this question have been fiercely debated. However, Smith quoted the Corps' definition, which is: "Areas saturated or inundated by ground or surface water, at a frequency and duration sufficient to support, and, that under normal circumstances, do support a prevalence of vegetation typically adapted for life in saturated soil conditions."

Smith also explained that despite various amendments, as set forth in the Clean Water Act of 1977, the discharge of dredged or fill materials on wetlands remains under the jurisdictional responsibility of the Corps. Presently, WES is cooperating with researchers to aid in the technical definition of jurisdictional boundaries. Smith noted that the rationale of "404" jurisdiction of wetlands remains valid, among other reasons, because such lands "are an important part of the hydrologic cycle."

Many activities

Environmental activities, many and varied though they may be, are only a part of WES' mission. Other work there includes research in hydraulics, soils, mobility, blast effects, and construction materials. For example, scale models of various dam or lock structures, and their surrounding waters, along the Mississippi River or its principal tributaries, are made, in order to determine optimum configuration. In another area of the station, explosive effects on structures are evaluated.

So, in many ways, WES is a unique installation for military and civil works, including environmental studies. A visit there is definitely worthwhile. *ES&T* extends to WES congratulations on the occasion of its 50th anniversary, and best wishes for the next half-century. JJ

Pulse the precipitator . . .

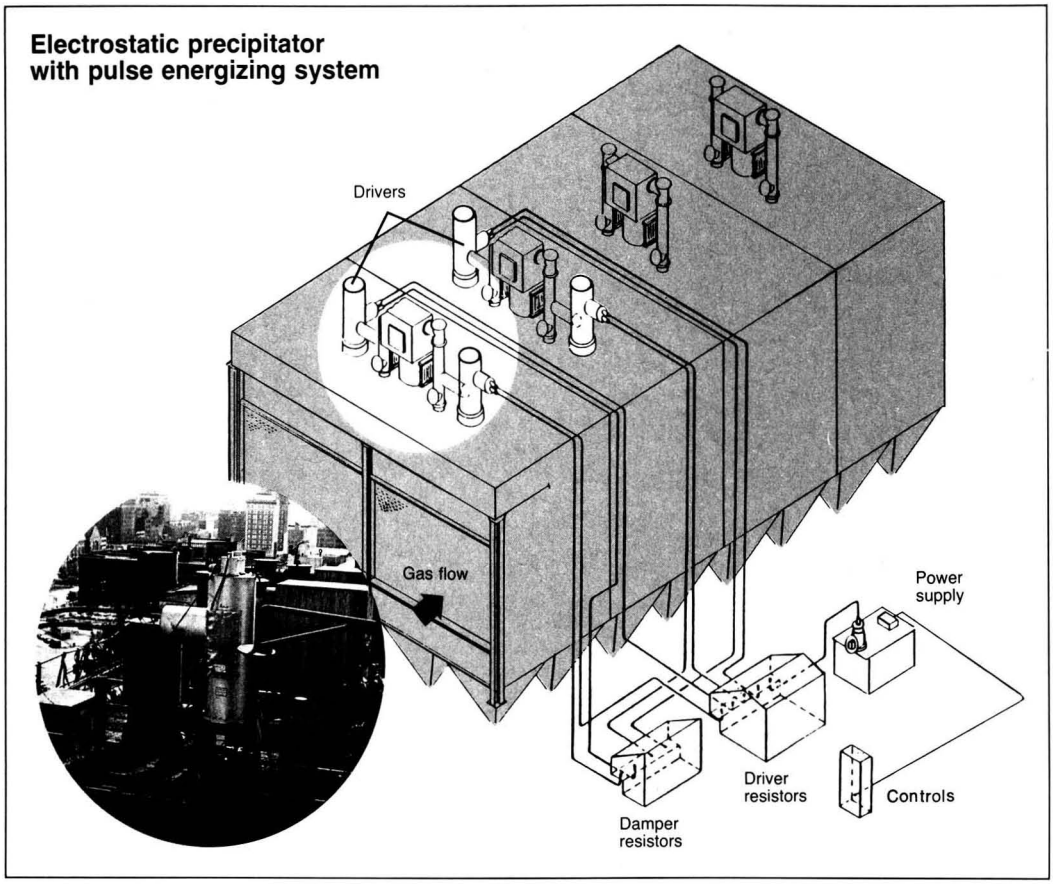
. . . With a recently developed system to enhance its efficiency to collect high resistivity fly ash

Research-Cottrell (Somerville, N.J.) and High Voltage Engineering Corp. (Burlington, Mass.) have announced a major improvement in electrostatic precipitator technology. They spent nearly $2.3 million over a 5-year period to develop what they call a pulse "energization" system. They claim that it "enhances the performance of precipitators under a wide range of operating conditions," and is cost competitive with baghouses.

The concept is not new. Research-Cottrell has worked on pulse energizing systems since the late 1940's, as has its major competitors. Until now, however, the hardware needed to translate theory into practice was too primitive. With the development of a reliable all-electronic pulse system, a full-scale prototype, and then commercial units, could be placed in operation.

At a June 20th press briefing, Research-Cottrell's president Dennis Carlton-Jones said: "We look to pulse energization as a means of increasing the precipitator share of the particulate control market for new equipment. Additionally, we see the development of an immediate short-term retrofit market due to the system's ability to significantly improve the performance of existing precipitators handling particulate emissions from low and medium sulfur coals."

At the same briefing, the company also announced the receipt of its first order, for $5.6 million, from an un-



named southeastern electric utility to retrofit and upgrade two existing precipitators to 99.3% efficiency. (The pulser systems alone cost $2.3 million.)

How it works

The reason existing units can be retrofitted is that the pulse energizing system—a pulse power supply, a driver unit consisting of charging and coupling capacitors, an electronic switch, air-cooled driver and coupling resistors, and controls—is merely coupled to the existing precipitator energizing system with no mechanical changes made to the precipitator itself. The added system superimposes high-frequency pulses of short duration on the normal negative 60-cycle energizing voltage wave form.

The addition of high-frequency pulses to the normal base wave form results in higher instantaneous peak electrical fields, more effective particle charging and, therefore, more effective particle collection. The pulse energizing system increases the so-called enhancement factor—the ratio of pulsed to unpulsed effective migration (or particle collection) velocities. As the enhancement factor increases, the size of the precipitator required to do a given job decreases.

Until the pulse energizing system was developed, SO_3 conditioning was the only logical alternative to conditioning high-resistivity ashes produced from low-sulfur coal. Fortunately, the enhancement factor appears to share a direct relationship with ash resistivity: as ash resistivity increases so does the enhancement factor.

Thus, a precipitator requiring a specific collecting area (SCA) of 600 could be sized at 300 SCA with a pulse energizing system that had an enhancement factor of 2. Enhancement

R-C's Dennis Carlton-Jones
a means of increasing market share

factors in this range (1.22–2.09) were achieved at one of Research-Cottrell's testing facilities, a 35-MW coal-fired boiler at the Perry K. Station of Indianapolis Power & Light Co., which provides steam to downtown Indianapolis, Ind.

At this installation, coal with sulfur content varying from 0.6–1.2% was burned; ash resistivity ranged from 5×10^{10} to 5×10^{11} ohm-cm, and enhancement factors of 1.22–2.09 were achieved. Stack opacity was reduced by 50% during one burn.

This performance was achieved with a simple and, according to Research-Cottrell, reliable pulser system that utilizes a gas submerged pulse gap at relatively low-pulse-repetition rates. And according to Research-Cottrell, this is not a "minor hardware improvement," but one which makes all precipitators more reliable and cost-effective.

Implications

The Electric Power Research Institute (EPRI), a utility-sponsored organization, is taking a "wait-and-see" attitude until independent tests corroborate Research-Cottrell's findings. EPRI and Research-Cottrell are now negotiating a joint testing/evaluation program, which may take place early next year at that unnamed southeastern utility.

EPRI's Walter Piulle, project manager, air quality control for fossil fuel power systems, told *ES&T* that should the independent evaluation confirm Research-Cottrell's claims, the pulser system would indeed be "a major contribution to the improvement of electrostatic precipitators."

Indeed it would. The pulse energizing system would then release the yoke that binds precipitator performance to fuel composition and operating temperatures, parameters that determine ash resistivity. Furthermore, because the system increases collection efficiency, the size of precipitators can be reduced, with obvious savings in capital and operating expenses. LRE

Sets of air facts

Attendees at the APCA (Air Pollution Control Association) meeting hear the clarion call for resolution of data sets

Why, O why O, did it ever leave Ohio? After an absence of 29 years, APCA held its 72nd annual meeting in Cincinnati. Today, Steubenville, Ohio, once one of the dirtiest cities in the U.S., has reportedly reduced its levels of particulate matter 55% and of sulfur dioxide 33%. Further, legislation is being prepared to introduce a transportation I&M (inspection and maintenance) program in the state. What's more, there is a new nuclear plant going in at Moscow, Ohio.

Sen. Gary Hart, chairman of the National Commission on Air Quality, said, in his speech at the meeting, "Everybody wants clean air, but people disagree sharply over almost every single policy issue." He explained that people disagree on policy questions largely because they do not agree on the facts in debate. For example, he noted that there is no consensus on such basic questions as:

- What levels of pollution endanger public health?
- Does technology exist to cut emissions a certain amount?
- How does pollution control affect the economy?

The problem is not a lack of information. Indeed, it often seems that every group has its own complete set of

facts. The problem is the conflict among all the "facts" in the debate.

Growth issue

In his keynote address, R. W. Baldwin, president of the Gulf Oil Refining and Marketing Company, said that growth and clean air are what this meeting is all about. Baldwin said, "Some aspects of air pollution control are getting in the way of growth, and in very real terms, this country is dying as a result of that."

He reminded the attendees that the expressed intent of the Congress in passing the Clean Air Act of 1970 was, "To protect and enhance the quality of the nation's air resources so as to promote the public health and welfare and the productivity of its population." In his view, it is necessary to note that cost is one of the ways in which one measures productivity. He noted that during the 1950-73 period, U.S. productivity grew at an average annual rate of 2.7%. Since 1973, that rate of growth has fallen by one-half. "Last year it hit an abysmal 0.4%," Baldwin said.

He said that studies have shown that in 1975 alone, environmental control costs reduced our potential growth in output from existing capital and labor by more than 11%. "Within the last decade, more than 30 refinery projects have been announced at various locations on the East Coast," Baldwin said. "Primarily because of environmental concerns, none has been built. There has not been a new refinery brought on-stream on the East Coast since 1956.

"Regulations have been developed by the EPA and DOE which could delay start-up of new construction by close to five years," Baldwin continued. "We are already seeing the beginning of project cancellations because certain areas are so locked-up by regulations. Dow Chemical, for instance, has decided to build a major petrochemical plant in Saudi Arabia, since—after two years and $40 million—permission to build a similar facility in Northern California was denied . . . even though the local pollution control authorities conceded that the company's initial plans called for just about the cleanest plant of its type.

"I think the fundamental challenge to economic growth emerges from the act itself and, therefore, correction is a Congressional responsibility. One cannot imagine the House and the Senate setting out to consciously harm the American economy. These things are done as a by-product of single-purpose legislation which fails to take into account the impact of other national aims and goals," Baldwin said.

In conclusion, he noted that he would recommend that the APCA prepare some appropriate recommendations to the National Commission on Air Quality on the effects of the Act on industry.

Gathering data

As Chairman of the National Commission on Air Quality, Sen. Hart noted that one of the prime efforts of the Commission is to resolve some of the conflicting facts and arguments about air quality. Having adopted its official study plan on June 22, the Friday before the APCA meeting, the Commission aims to give to the Congress and to the public fair, balanced, and accurate information on air pollution and our efforts to control it. Its first report is due next August.

Keynoter Baldwin
concerned with effects of the Act on industry

Commission's Sen. Hart
resolving conflicting facts about air quality

A case in point is the recent controversy over new standards for power plants (*ES&T,* February 1979, p 172). "Some environmentalists argued for 95% pollution reduction, saying 'wet scrubbers' have been proven to remove that much pollution," the senator says. "Some coal companies argued for a 35% standard, saying that it is impossible to do better with proven technology. Different groups of people push very different policies, presenting very different representations of the facts," Sen. Hart explains.

For John Q. Public, of course, billions of dollars and billions of tons of pollution are at stake. Indeed, the desire for better information was a major reason that Congress created a special commission.

The Commission will have served a major purpose if it does nothing more than compile and evaluate information, according to Sen. Hart. Also it can help in another way. That is to suggest to the Congress how to improve air quality with less regulatory burden and frustration.

Prognosis

The public continues to support better air quality but is rebelling against inefficient government regulation. Everywhere Sen. Hart goes he says he meets people frustrated with government regulations. It's true that the clean air program is the single most expensive regulatory program. CEQ says this nation will spend over $213 billion between 1977 and 1986 meeting clean air standards. But the Clean Air Act has made a major difference, according to the senator. "Over 90% of our factories are complying with air pollution standards," Sen. Hart says. "Pollution from individual cars has been reduced substantially. Still, these changes have just kept pollution from getting worse, rather than leading to actual improvements."

How far have we come on this road to clean air? EPA's measurements confirm how little progress we have made. The senator said, "Four of the five major regulated pollutants have been reduced. But only one of the nation's 102 largest cities has healthy air. A new study shows visibility has declined 10-40% across the nation."

At the bottom line, a major challenge during the next Congressional review of the Clean Air Act will be to satisfy both of these popular demands: clean air and less burdensome regulations.

Another challenge is finding out how best to increase production of coal and other domestic energy resources while preserving air quality. For example, the Commission will study how the new provisions to protect clean air regions affect power plant siting and construction. So far, Sen. Hart said, "EPA has approved 74 new permits for coal-fired plants in clean air regions, while rejecting only two. This early record strongly suggests the law does not inhibit energy production."

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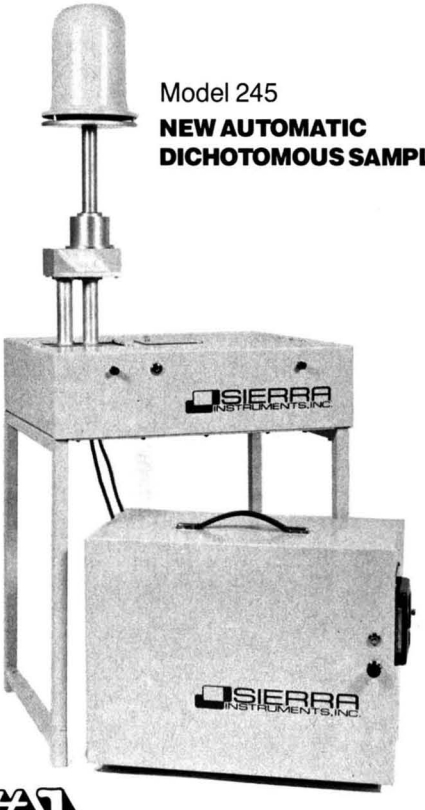

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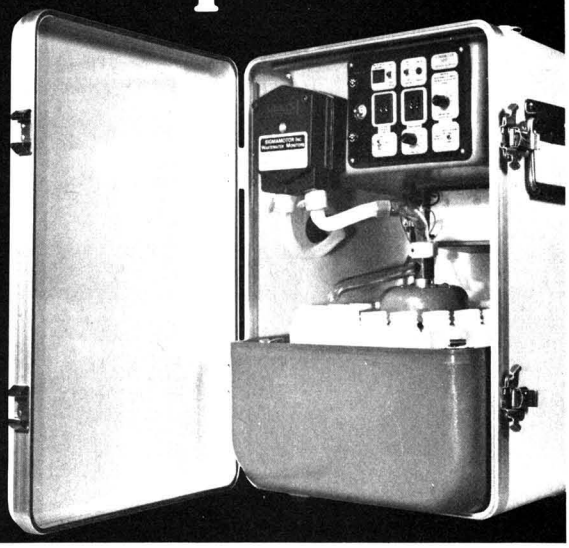

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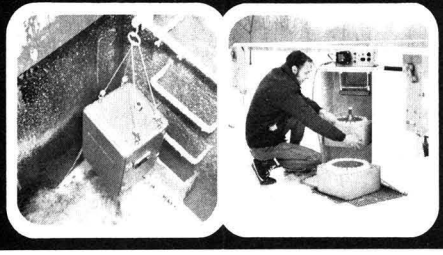

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PSD regulations: the final round?

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A little over a year ago, the EPA published final regulations for preconstruction review of major new or modified sources under the prevention of significant deterioration (PSD) provisions of the 1977 Clean Air Act Amendments (*Fed. Regist.*, **43**, 26380, June 19, 1978). Industrial groups and environmentalists promptly petitioned for judicial review; briefs were prepared and the case argued on an expedited schedule.

In June, the Federal Court of Appeals for the District of Columbia Circuit announced its preliminary decision in which it invalidates or questions many of EPA's regulations (*Alabama Power Co.* vs. *Costle*, June 18, 1979). Thus, yet another period of open debate and administrative decision making lies ahead, and persons working with the PSD program face continued uncertainty about what the law requires.

In the ensuing months, be alert both for changes in the operation of the PSD program and for opportunities to participate in revising the regs.

Key provisions affected

Among the plethora of issues the PSD litigation raised, several of general significance merit mention. Only "major" sources are subject to preconstruction review, and the Act defines "major" sources in terms of their "potential to emit" certain amounts of pollutants.

The court held that the potential to emit should be calculated after accounting for the effect of the air pollution controls incorporated in the plant design. Since EPA's rules had ignored the effect of these controls, this will substantially reduce the number of smaller sources needing permits. In the case of a modification to an existing facility, the court adopted a strict reading that a modification causing *any net* increase in emissions must be reviewed.

The rigor of this requirement is softened by another part of the opinion stating that any reductions in emissions at other points in the source may be offset against the emissions from the modification in determining the *net* increase in emissions. If there is no *net* increase, no PSD review is needed.

Although the court's decision reduces the number of sources subject to PSD review, it significantly broadens the scope of that review. In repeated statements, the court declared that the PSD review should embrace the emissions of any amount of any pollutant regulated by the Clean Air Act. This includes hazardous air pollutants (e.g., benzene) and pollutants that may be regulated in one or another new source performance standard (e.g., total reduced sulfur), as well as the criteria pollutants.

Two corollaries follow:

- Pre-application ambient air quality monitoring should be performed for all pollutants.
- The applicant must define best available technology (BACT) for all pollutants.

On other issues of general significance, the court approved EPA's modeling guidelines, its rules on adjustments for tall stacks, and its interpretation of PSD increments as absolute ceilings. The court remanded EPA's definition of "source" but advised EPA that the new definition could legitimately include "common sense industrial groupings." The court also remanded the rules for applying the PSD program to surface mines and other sources of fugitive dust, but supported EPA's fundamental authority to regulate such sources.

EPA has the next move

The constitutional limits on the authority of the judiciary compelled the court to remand the invalidated portions of the regulations to EPA to reconsider in the light of the court's opinion. Where the court's opinion is specific EPA has little choice, but many of the holdings will require new exercises of agency discretion.

Pre-application monitoring requirements are one example. The court says the Act requires monitoring of all pollutants, but EPA may find that there is no method for monitoring some pollutants, or that the amount of emissions from some plants is so small that monitoring is meaningless.

To sort out all these issues will take time. Some of them, like monitoring, present new policy choices calling for complex technical and policy judgments. Once EPA has formulated policy proposals internally, the important but time-consuming procedure of published proposal, hearings, comments, and final rule making ensues. It will be late this year or early 1980 at least before EPA will adopt final regulations in response to the court's decision.

Problems of transition

At EPA's request, the court stayed the effect of its preliminary decision, leaving EPA's existing regulations in force. Until further notice, EPA will continue to process PSD applications under the existing regulations. However, because the court may decide to make some parts of its decision retroactively effective the PSD permits now contain a warning that they are subject to modification.

A major area of uncertainty is how the court's decision will affect state PSD programs. Most states have already devised PSD review programs in keeping with the existing regulations, and EPA was prepared to turn over the PSD program to the states. Must the states now rewrite their rules, too? May EPA approve state PSD programs that satisfy the existing regulations? No answers to these questions have yet emerged. To compound the confusion, most of these state programs are already in full force and effect as a matter of state law. Sources may thus be subject to both state and federal PSD reviews, which may impose inconsistent requirements.

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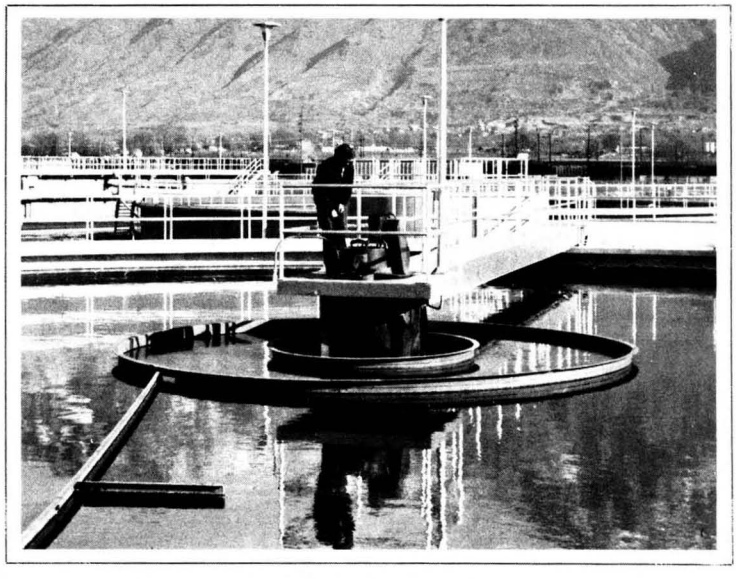
ES&T
FEATURES

The market for water management chemicals

Here is a look at what it consists of, what its present trends are, and which way it could go in the next several years



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The use of chemicals in treating potable, internal, and waste water is favored by several factors, including economic, technical, and political considerations. Indeed, on net balance, one can argue that chemical treatment is an attractive proposition, when compared to capital expansion. Table 1 shows capital and operating costs for selected population and plant sizes as of 1977-78. Depending on these factors, level of treatment desired, and other conditions, cost of cleanup will vary from under 10¢/1000 gal to over $2/gal, truly a wide range.

There are also major cost variations among industries, and even within an industry, depending on pollutants, local rules, and so on. In the pulp and paper industry, for example, the activated sludge process is about three times as costly as lagoon aeration per 1000 gal handled, and per lb of BOD removal. Scale of plant is significant, and costs per gal of a 1-mgd facility might be twice that of a 100-mgd unit. However, the economies of scale are not as significant, as the size of the plant increases.

Primary physical treatment is cheaper than secondary chemical and biological treatment. But advanced water treatment (AWT), such as reverse osmosis and electrodialysis, is currently very expensive. Typical costs per 1000 gal at a large facility are as follows:

- primary treatment—8-10¢
- secondary treatment—10-20¢
- tertiary treatment—12-25¢
- quaternary treatment—25-85¢.

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Since secondary treatment follows primary, and so on, costs are cumulative. Thus, costs of complete treatment would range from 55¢, minimum, to $1.40 or more per 1000 gal. In addition, sludge disposal costs are estimated at anywhere from 3 to 95¢ per 1000 gal treated.

Nature of the industry

The water treatment chemical industry is highly fragmented and highly diversified. Hundreds of manufacturers are involved in selling bulk and specialty chemicals for incoming, internal, and outgoing water treatment. However, only a handful of companies derive a significant share of their business from the sale of chemicals for such end uses.

Companies selling chemicals must keep in mind that their markets are also highly fragmented. The most frequent division is that between municipal and industrial markets. Also, there are further variations within each, in terms of size of installation, nature of industry or operation, pollution problems, incoming water quality, and the like. It is possible to identify yet other markets, for example, households and farms. Suffice it to say that manufacturers face a difficult problem in locating, capturing, and retaining major users. However, once such markets are found, it is possible to build loyalty by providing consulting and maintenance services.

Successful operation in this industry requires the following two major conditions:

- experienced scientific, technical, managerial, and sales personnel to satisfy both users and regulating authorities
- a systems approach to marketing, with due recognition of the importance of "software" and services.

Types of companies

Many large-, medium-, and small-sized firms make up the water treatment chemical industry. While the majority of such firms are listed in "SIC 28—Chemical and Allied Industry," there is good representation from other major industries, such as "SIC 35—Non-Electrical Machinery." Five major types of organizations can be distinguished; this classification is based on a combination of corporate size, "market reach," product line, and ownership.

First, there is the family of very large manufacturers, those with sales in excess of $1.5 billion. These giants of the field are well-known: Allied Chemical, American Cyanamid, Borden, Celanese, Dow, DuPont, W. R. Grace, Hercules, Monsanto, Olin, PPG, and Union Carbide. However, profit margins for these companies eroded from 1974 to 1977, mostly because of global economic problems.

These firms, while well-diversified, tend to engage in the manufacture of bulk, rather than specialty chemicals. Nevertheless, some of them are beginning to pursue segments of the water treatment market. Consider these two examples: Hercules now offers a line of flocculants, biocides, and internal water preparations, and also designs advanced waste treatment

Use of chemicals for wastewater treatment: Some positive factors . . .

- Chemicals are often cost-effective when compared to the cost of land, labor, and capital—all needed when the choice is that of equipment. Users have also recognized that it may be wiser to spend on current account when capital funds are in short supply, when interest rates are high, or when innovation is fast changing the industrial processes utilized in a given plant.
- Although prices of chemicals rose sharply during 1973–75, they appear to have levelled off, and current price increases do not exceed the rate of increase for equipment. Furthermore, substitution possibilities encourage intercompound competition.
- Use of water treatment chemicals can result in substantial fuel savings, especially in the case of internal water treatment. The thrust of energy costs is the single most significant factor on the market for water treatment chemicals. Plant engineers are recognizing, contrary to previously held beliefs, that energy and environment are partners, rather than enemies, in inflationary times.
- There is increased per capita consumption of water. There is also increased demand for high-quality water. The use of chemicals is a factor in both trends.
- Increasingly tighter effluent standards require nontoxic wastewater, reduction of sludge, and the like, all of which necessitate greater use of chemicals.
- Despite some population movement to rural areas, this country remains an urban one. Ground water must be conservative in urban, suburban, and rural areas. Thus, increased reliance on treated rather than well water can be expected.
- Manufacturers of water treatment chemicals are willing and able to spend research/development dollars for new, more effective compounds. The rate of innovation in this area seems as good as that in the equipment field.

. . . and some negative factors

- A definite trend exists in industry toward recycling, that is, reclaiming and reusing water, with the result that less chemical dosage will be needed. However, while such internal water remains relatively clean, it must still be treated chemically, and partially replaced, in order to prevent scale and corrosion.
- Prices of chemicals, especially organic chemicals, have risen sharply; some increases during 1973–75 were on the order of 100%, 200%, or even more. In such instances, users will seek cheaper substitutes, or even eliminate certain production lines.
- There is a definite concern about using chemicals for cleaning water, when these very same chemicals can be, or are, classified as pollutants. This is especially true in the case of complex organic compounds, but is the case also for aluminum sulfate and ferric chloride.
- In order to save energy or avoid cleanup costs, some companies are shifting to new facilities with built-in pollution control equipment, and with built-in water conservation features.
- Although commercial office building construction will continue to increase at the rate of about 4% per year in constant dollar terms, more efficient air-conditioning systems will be designed, thereby slightly reducing the need for cooling water compounds.
- Federal grants, managerial attitudes, and consulting engineers' fees still tend to favor capital-intensive projects at the expense of operating or current accounts. This situation is changing—slowly, but perceptibly.

TABLE 1

Comparison of capital and operating costs for selected wastewater treatment alternatives, 1977–78

Population (thousands)	Plant size (mgd)	Capital costs[a] ($000)		Operating costs[a] ($/mg)	
		Capital expansion[b]	Chemical treatment[c]	Capital expansion[b]	Chemical treatment[c]
		A B	C D	A B	C D
25	2.5	70–210	8–16	14–54	9–29
250	25	240–1340	23–43	4–35	5–23
500	50	475–2850	38–75	3–33	4–20

[a] Incremental to existing costs; exclusive of collection and disinfection systems.
[b] Range: A = clarification, B = clarification and aeration.
[c] Range: C = flocculation, D = flocculation and coagulation.

Sources: 1. Based primarily on Stacy L. Daniels et al., in *Water—1976: Physical, Chemical Wastewater Treatment*, Gary F. Bennett, Ed., American Institute of Chemical Engineers, New York, 1977, pp 333–342.
2. Updated and adjusted for population and plant sizes shown here by the author, based on conversations with pollution control analysts and municipal and industrial authorities.

systems, including a dewatering/incineration unit. A multinational firm, Hercules, in the 1970's, acquired Oceanchem, Kedea AB, and Genu Products, all outside the U.S.

Olin, a diversified manufacturer offering many basic chemicals, established a Water Services Division that is recording sharply rising sales and income figures. Key products offered include chlorine dioxide, catalyzed hydrazine, and swimming pool chemicals.

The second group consists of medium-sized chemical manufacturers, those in the $20 million–$1.5 billion sales volume range. Included in this group are both general and specialty manufacturers. Examples of the former are Air Products and Chemicals, Morton-Norwich Products, and Pennwalt.

Take Pennwalt as an example: Its product line falls into three major categories—chemicals, health-related products, and specialized equipment. It offers a broad range of chemicals; those items with applications in water treatment include caustic soda, chlorine, activated carbon, and organic coagulants. The production of calcium hypochlorite has just been discontinued because of lack of profitability. Pennwalt offers a water pollution control equipment line ranging from pumps and chemical feeders to centrifuges and flow meters. Its operations are carried out in 97 plants located across the U.S. and 18 other countries.

"Handholding" is wise

The specialty manufacturers in this second category can be further subdivided into two groups—those with heavy emphasis on chemicals intended for water and wastewater treatment and those who stress their lines of cleaning-sanitizing chemicals. The former group encompasses the family that was affectionately labeled the "Big Six Pack" (*ES&T*, May 1974, p 414). They are: Betz Laboratories; Chemed, 90% owned by W. R. Grace; Mogul, recently acquired by Dexter; Nalco Chemical; the Calgon division of the giant pharmaceutical company, Merck; and U.S. Filter with its Drew Chemical Division.

The "maintenance chemical firms" are represented by Economics Laboratory and Diversey, which was bought by Molson Breweries of Canada. They have a definite interest in pollution control chemicals, and it would not be surprising to see them pursuing this market more aggressively. As a general rule, specialty chemical makers show a higher rate of return on sales than do the multibillion-dollar firms. Close attention to the problems of clients, coupled with a systems approach, has developed strong loyalty among their customers. "Handholding" is a good rule—for example, Mogul even assists clients in filling out forms to meet regulations.

The third category consists of manufacturers from other industries, especially machinery and equipment makers, for whom the decision to enter the water/wastewater treatment chemical field was a natural diversification. Examples are Clow, Eagle-Picher, and General Signal.

Eagle-Picher's diatomaceous earth filter-aids are widely used for high purity applications. Clow, best known for its cast iron, plastic, and vitrified clay pipes, is the parent firm of Vulcan laboratories, maker of cooling water and related compounds.

Some other major companies, such as General Refractories, Petrolite, and Westvaco, have chosen to enter the market with a single product, in some cases with multiple and even unrelated products. A good example is Westvaco—a paper and packaging products firm—which is the leading producer of activated carbon, with its 4 million lb/y capacity. Should the Environmental Protection Agency (EPA) insist that all drinking water be carbon filtered, Westvaco would reap significant benefits.

The fourth category consists of small chemical companies, those with sales of about $1–20 million. These firms usually specialize in a group of related chemicals, such as boiler feed, water softening, or swimming pool products. Most of these firms function in the area of internal water preparations, and many tend to be privately owned. Examples are Alken-Murray, Mitco, and Garratt-Callahan.

Alken-Murray appears to be a regional firm, operating chiefly on the East Coast and in the Midwest. On the other hand, Garratt-Callahan operates plants in California, Texas, Illinois, and Georgia, and maintains at least one technical sales representative in each state.

The fifth category is a new one—it consists of foreign companies that have entered the U.S. water treatment chemical market in increasing numbers during the mid- and late 1970's, often through the acquisition route. Examples are Lonza AG of Basel, Switzerland; Imperial Chemical Industries, purchaser of Atlas Chemical, an activated carbon manufacturer; Norit NV of the Netherlands; Mitsubishi Chemical; and, as mentioned already, Molson Breweries of Canada, buyer of Diversey. U.S. firms can expect competition in the future from these and other German, Swiss, British, French, and Japanese organizations.

Size doesn't assure profits

In the water management industry, size alone is no assurance of high profits. Both large and small companies can have poor performance records. Indications are, however, that the best profit records continue to be shown by medium-sized firms. Those firms are large enough to operate under a systems approach and with a well-trained research and sales staff, yet small enough to specialize and carve out selected segments of the total market, be it by geographic area, type of compound, or type of client.

There are contrasting trends at any given time in the water treatment chemical industry; some firms enter, others leave. Some drop product lines, while others add new ones. There is a trend toward discontinuing unprofitable basic chemicals. For instance, Diamond Shamrock stopped making soda ash (synthetic soda gave way to the natural deposits from Wyoming).

Mergers and acquisitions have been taking place in this field at a rate equal to that of other segments of the chemical industry, or U.S. industry in general. Within the past 2 years, one could read about the following mergers (with acquiring company listed first): Beatrice Foods—Culligan International; Dexter—Mogul; Essex Chemical—Racon; Kennecott—Carborundum; and Molson Breweries—Diversey. Most recently, BOC International of England claimed "full indirect ownership" of Airco, and Pennwalt purchased Barnebey-Cheney.

Table 2 shows a list of selected large, medium, and small firms whose product line includes both bulk and specialty chemicals for the treatment of intake, internal, and effluent water. Of the companies shown, only a handful derive one-fifth or more of their sales from the sale of water management chemicals (such as Betz, Garratt-Callahan, Nalco). It is expected that the most pervasive trend for all the firms in the list will be diversification. Target marketing and building brand loyalty will remain key objectives.

There will also continue to be a direct relationship between size of the supplier and size of the end user. Thus, Nalco Chemical deals with the very largest paper, steel, and chemical process manufacturers, while Alken-Murray would focus on small clients. Finally, one can expect mergers and acquisitions to continue, possibly even at an accelerated pace.

Shipment trends

Shipments of water management chemicals were 5 billion lb in 1960, nearly 17 billion lb in 1977, and are projected to approach 47 billion lb by 1990, a growth rate of more than 8% per year. Values of shipments were $175 million in 1960, $1.3 billion in 1977, and are forecast to rise at an 11.6% annual rate, exceeding $4.5 billion by 1990. Currently, about 200 lb of chemicals are being consumed per million gallons of municipal and industrial water use; this figure should reach almost 500 lb by 1990. Table 3 shows the major categories of chemicals, by physical units and dollar terms, in 1960, 1977, and 1990, as well

TABLE 2
Selected water treatment chemical companies

Company	1977 Employees (thousands)	1977 Sales (millions of $)	1977 Net income (millions of $)	1972 Sales (millions of $)	1972 Net income (millions of $)
Airco	14.5	837.4	54.0	492.3	18.0
Air Products and Chemicals	13.7	947.2	67.7	351.2	18.3
American Cyanamid	43.8	2412.3	139.4	1358.9	108.8
Betz Laboratories	1.8	148.3	15.9	57.3	4.6
Carus	0.5	25.0[a]	n.a.	20.0[a]	n.a.
Chemed	5.7	286.4	20.0	140.0	10.4
Chemtrust Industries	0.5	14.0[a]	−1.0	11.4	0.2
Clow	2.7	141.4	3.7	105.9	5.1
Dexter (Mogul)	4.8	315.8	18.5	66.2	4.0
Diamond Shamrock	11.3	1530.4	162.1	617.3	33.3
Diversey	4.1	130.6	4.1	58.8	1.8
Eagle-Picher Industries	10.2	474.0	26.0	255.9	11.8
Economics Laboratory	5.7	358.6	23.4	154.3	9.7
Essex Chemical	0.6	76.8	4.1	37.5	0.7
Fairmount Chemical	0.1	8.1	0.4	4.4	−0.0+
Garratt-Callahan	0.3	11.0[a]	n.a.	9.0[a]	n.a.
General Refractories	8.0	344.2	−0.01	179.4	1.4
Hercules	24.5	1697.8	57.9	932.0	70.4
Ionics	0.5	29.1	1.6	10.5	0.4
Johns-Manville	25.4	1461.4	102.6	796.3	49.3
Merck (Calgon)	28.1	1724.4	290.8	958.3	147.6
Morton-Norwich Products	10.9	609.3	31.7	367.8	24.4
Nalco Chemical	4.2	445.6	50.1	194.7	20.1
NCH (National Chemsearch)	5.9	198.6	18.6	82.2	8.1
Oakite	0.9	52.1	3.4	30.5	2.2
Olin	22.0	1472.5	78.1	1098.3	30.2
Pennwalt	13.9	834.9	41.7	441.0	16.0
Petrolite	1.7	143.6	16.1	55.8	4.4
Rohm & Haas	13.0	1123.9	43.2	618.6	46.4
Stauffer Chemical	13.0	1232.7	116.0	542.6	33.5
Sybron	15.5	584.7	27.3	356.3	19.8
U.S. Filter (Drew)	6.0	423.7	13.9	123.0	6.2
Virginia Chemical	2.9	104.3	9.6	44.1	1.2
Westvaco	15.9	1000.6	61.9	472.0	13.1
Witco Chemical	5.0	632.4	24.6	293.5	12.6

[a] Estimated
n.a. = not available.

as their respective growth rates.

Bulk or basic chemicals will exhibit the slowest growth rate in the coming years, while biologicals—especially oxygen—and internal water preparations will enjoy the fastest percentage increases. The most significant trend, hidden in Table 3, is that of upgrading—begun in the 1970's, it is expected to last well into the 1980's. Thus, sales of organic coagulants will grow more rapidly than sales of inorganic ones; the higher prices of the former will be offset by their better effectiveness in both water clarification and sludge conditioning. Similarly, activated carbon markets will show a higher growth rate than those of simple filter media; ozone and oxygen use will be rising much faster than use of inorganic biologicals.

As for internal water preparations, the trend is toward nontoxic, nonpolluting chemicals, and toward those compounds that are effective not only in water treatment, but in energy savings as well. A good example of the latter trend is the family of synthetic dispersants, which offer better solid dispersion, as well as providing cleaner heat transfer surfaces.

Families of chemicals

There are five families of water management chemicals; some experts would choose fewer, or more, while others would object to the groupings listed here. They are: coagulants and flocculants; filter media of all types; neutralizers and salts; biological action chemicals, including oxygen; and internal water preparations.

Coagulation is the process whereby suspended solids and colloidal materials in the water are agglomerated into masses sufficiently large to settle; this is an irreversible chemical action.

Flocculation is the aggregation of suspended solid particles in water; it is a reversible process, as the cohesive forces are quite weak. Yet, for practical purposes one can treat the two processes or groups as one family. The four coagulant/flocculant family members are alum, iron, salts, other inorganic coagulants such as bentonite and kaolin, and organic coagulants such as natural and synthetic polymers.

The most significant development in this field is the combination of inorganic coagulants with organic ones for very effective action. Both types will continue to be used, though the demand for organics will grow far more rapidly, as they are effective in clarification and sludge conditioning.

Municipalities still use more coagulants than industries do, and more coagulants are consumed for potable water than for sewage treatment. However, industrial treatment should grow more rapidly than municipal, and sewage treatment more rapidly than water clarification.

Average prices of coagulants/flocculants at the manufacturers' level stood at 4¢/lb in 1970 and 9¢/lb in 1977, and should rise to 17¢/lb by the end of the 1980's. Prices of organic coagulants are now in the $0.50–3.00 range, but the specific price will vary according to volume purchased and transport costs.

Filter media

In water and wastewater treatment, filter processes remove contaminants from the flow by mechanical, chemical, or electrical means. Filtration is done in addition to coagulation and sedimentation when water is to be used for drinking and for internal purposes in the plant. Filter media include sand, zeolites, diatomite and perlite, activated carbon, ion exchange resins, and other materials. Filters may be used in tandem; for example, sand or coal is put in front of activated carbon beds, which are placed ahead of ion exchange resins.

Activated carbon is the filter medium dominating the news. It can be used to adsorb traces of chlorine and other oxidants, as well as to collect dissolved organic chemicals. If the EPA insists that cities with populations

TABLE 3
Shipments of water treatment chemicals

Item	1960	1977	1990	% Annual growth rate Historical	Projected
Millions of pounds					
Coagulants	850	2210	4050	5.8	4.8
Filter media	338	787	1650	5.1	5.9
Neutralizers & salt	2925	9270	17630	7.0	5.1
Oxygen		2200	18500		17.8
Other biologicals	496	1556	3162	7.0	5.2
Internal water preparation	307	920	1880	6.7	5.7
Total	4916	16943	46872	7.6	8.1
$/lb	0.035	0.078	0.118		
Millions of dollars					
Coagulants	24.8	187.7	684	12.6	10.5
Filter media	23.7	154.0	583	11.6	10.8
Neutralizers & salt	26.6	198.6	592	12.5	8.8
Oxygen		26.0	425		24.0
Other biologicals	37.4	282.1	1162	12.6	11.5
Internal water preparation	62.0	475.0	2070	12.7	12.0
Total	175.5	1323.4	5516	12.7	11.6
Water use (trillion gal)	69.6	86.4	95.0		
lb/million gal	71	196	493		
GNP (billions of $)	506.0	1889.6	5370	8.1	8.4
$/000$ GNP	0.34	0.70	1.03		

of 75 000 or more use activated carbon to remove trihalomethanes, then usage would skyrocket. But some experts contend that EPA is overstating the beneficial aspects, and that competing materials at lower cost are available. However, despite excess capacity, producers are now gearing up for an expanding market. Prices of activated carbon, stable for some time, are now in the $0.25–0.75/lb range, and moving up.

Neutralizers and salt

Neutralizers are low-cost, high-poundage materials. Lime, caustic soda, soda ash, and sulfuric acid are among the top chemicals produced in the U.S. for these purposes, and prices are still in the 1–3¢/lb range. These chemicals, along with salt, are used in water management to provide a balance of ions, that is, to adjust pH, nutrient, and metal levels.

There will be intra-family competition in the future, with soda and acids showing gains at the expense of lime and salt. But as a family, neutralizers will exhibit the slowest growth rate, when compared to other water treatment chemicals. Simply put, even at the low prices cited, they are not a very good buy because of:

- lack of effectiveness when compared to alternatives
- side problems, such as the amount of sludge left over.

Of course, neutralizers will be used in relatively large quantities, but usage will be more in combination with other chemicals than by themselves.

Biocides

Chlorine, inorganic chlorine compounds, other biocides, oxygen, and fluorides alter the biological characteristics of water. As a family, they tend to be used in treating water supply, rather than wastewaters.

Chlorine disinfects, and biocides inhibit the growth of microorganisms. But while effective, many biological action chemicals are toxic to humans and aquatic life; serious concern has been expressed in regard to the carcinogenicity/mutagenicity of chlorination byproducts.

Nevertheless, chlorination will not be phased out suddenly. As one expert put it, any chlorine substitute must be a good biocide, cost effective, and responsible for fewer hazardous byproducts, and it must provide an easily measurable residual. Such a chemical is hard to find, though ozone is being touted as an effective alternative to both chlorine and hypochlorites.

Ozone and oxygen usage will rise rapidly in the 1980's, with both usually produced on site. Ozone is utilized in sterilization and in the oxidation of cyanides and phenols. Oxygen aeration offers more efficient BOD removal and improved sludge digestion and requires less space than alternative methods. The oxygen market is dominated by Union Carbide's Unox system, now marketed to both municipal and industrial users; competitors include Airco with its F30 and Air Products and Chemicals with its Oases system. Largely as a result of poundage growing faster than dollar shipments, the price of biologicals should remain nearly stable in the 7–9¢/lb range.

Internal preparations

Major waste problems encountered within factories, power plants, and commercial buildings involve corrosion, scale, fouling, foaming, and related trouble spots. Mechanical equipment or physical treatment cannot do the job of prevention; at best, action can be taken after problems are encountered. Magnetic action has been mentioned as a possibility to fight scale in pipes, and to soften water, but has not met with wide acceptance so far (because of an unfavorable, controversial report when first introduced).

Thus, chemicals remain the choice for internal water treatment. Chemicals sold for such tasks are highly specific, formulated compounds, usually containing several components. "The total package" must take into account supply water characteristics, nature of pretreatment, type of equipment used, level of expertise of operating personnel, product and process characteristics, and legislation by all levels of government. Therefore, the design of optimum packages is a complex task. A special segment of the chemical industry is serving users, a segment dominated by the "Big Six Pack." Of the $475 million worth of internal water preparations shipped in 1977, Nalco and Betz each accounted for about 21%, while the market shares of Chemed, Dexter (Mogul), Merck (Calgon), and U.S. Filter (Drew) fell in the 4 to 8% range.

The average price of internal water preparations should more than double between 1977 and 1990, rising from $0.50 to over $1.10/lb. Of the three major categories of such preparations, boiler compounds will lose, and cooling compounds will gain relatively, while process compounds will remain stable.

Who are the users?

End markets or users for water treatment chemicals include municipalities, industries, and even households and farms. To discuss each user segment is impossible within the scope of this paper. But it is instructive to touch briefly on one family, namely, coagulants, and describe three specific applications in the case of internal water preparations.

Coagulants in 1970 were used in the following proportions: municipal water treatment, 30%; industrial water treatment, 31%; municipal wastewater treatment, 31%; and industrial wastewater treatment, 8%. By 1980, the corresponding figures will be: 225, 32, 33, and 13%, truly a remarkable change (these figures are on a volume/weight basis, not on a dollar basis).

Why the change? Because both coagulants and users are changing. Coagulants and flocculants are changing in terms of technology, effectiveness, and price. Users are changing as a result of governmental legislation, self-regulation, and the nature of processes carried out in the plants. Currently, for example, several hundred municipal wastewater treatment plants are using inorganic chemicals for the precipitation of phosphorus and the reduction of suspended solids. At the same time, however, high molecular weight, synthetic flocculants are making inroads in this area, because they make gravity dewatering far more feasible.

The amount of internal water preparations needed for a given size building or industrial plant varies widely. Thus, the third case cited below indicates a usage rate of 1 lb of chemical compounds per 100 ft^2 in a large office building. But this figure cannot be called typical, as some skyscrapers generate their own water/steam, while others purchase the same from municipal sources. Accordingly, some building maintenance crews are called upon to add chemicals, while others buy the compounds only indirectly and play no active role.

One possible measure of the usage rate of chemical preparations is that about 3 gal of water is needed per ton of air conditioning, and about 2 lb of chemicals is needed for every 5000 gal of water. Generally, industry uses 3–15 lb of chemicals for every million gallons of water treated, but one can cite figures well beyond this range.

Yet other measures, relevant in 1977–78, are as follows:

- about $3–13 worth of boiler compounds used for every million pounds of steam
- about $0.50–2.25 worth of cooling tower compounds utilized for every 1000 gal of blowdown
- about 0.1–20 ppm of compounds

Three case histories

Case 1. In a major petroleum refinery, untreated water reached an 80% fouling rate every 21 days, because of high temperature, low velocity, and microbiological growth. Production had to be halted while units were mechanically cleaned. However, dispersant and microbiocide formulations by the Mogul subsidiary of Dexter, applied every 12 days, held the fouling rate below 30%, and kept equipment on line, with no significant production loss. Savings amounted to over $8000/mo. Other companies also offer cleaning of fouled systems on an on-stream basis, that is, without costly shutdowns. Basically, three steps are involved—precleaning of the recirculating system; pretreatment with corrosion inhibitors; and ongoing maintenance against corrosion, fouling, and microbiological action.

Case 2. A large textile manufacturer had a history of zinc phosphate deposit problems, when using a zinc organic base corrosion inhibitor plus dispersant, because of natural phosphate in the makeup supply water. The major problem was zinc fouling in cooling water condensers and inability to maintain adequate heat transfer. The condensers had copper tubes with mild-steel tubesheets.

The company switched to a new inhibitor, which was a combination of polyelectrolyte, organic corrosion inhibitor, and antifoulant, called Drewgard 193, made by the Drew Chemical subsidiary of U.S. Filter Company. The new compound was fed continuously at 75 ppm, without pH control, but with two microbiocides slug-fed to control microorganisms.

The new inhibitor removed the old zinc-based sludges and prevented further depositions. Corrosion protection was equal to that of the old program, with rates at less than 2 mils per year. No problems were found with phosphate deposition or bacterial control.

As in the first case, there is much competition in this field, especially among the "Big Six Pack" to capture such end users. Each firm claims very low corrosion rates, as well as low chromate content in its clients' plants.

Case 3. The Chicago Civic Center is a 1.46 million ft^2, 31-story structure, where equipment and machinery are operated by The Whiston Group. The water treatment must protect the boilers, condensers, refrigeration machines, cooling towers, and induction and reheat lines. There are 4 boilers with a total capacity of 220 000 lb of 120 psi steam per h, 5 centrifugal refrigeration units with 8200 tons of combined capacity, 17 high-pressure mains, 18 reheating systems, 35 fans that can move 1.8 million cfm of air, and 3 vertically induced cooling towers with a flow rate of 18 000 gpm.

The boilers use city water, softened by passing through sodium zeolite units. About 12 000 gpd of makeup water is needed, since 85–90% of the condensate is returned. Boiler feedwater is treated with a single package, multipurpose formulation that contains a precise ratio of ortho- and polyphosphates combined with organic dispersants, an oxygen scavenger, and a boiler water antifoam.

Condensate return lines are protected by a volatile, neutralizing amine corrosion inhibitor at a 7.2–8.2 pH range. A zinc organic base corrosion inhibitor protects the multimetal system from attack; scale and deposits are prevented by an organophosphonate type treatment ranging from 60 to 100 ppm.

Two microbiocides, alternated weekly, are used during the cooling period. A phenolic amine treatment is used to combat the formation of algae, fungi, and slime. The chilled water system and the forced hot water system are protected with a low-toxicity corrosion inhibitor, which contains a complex of borate–nitrite, plus organic inhibitors. A total of 14 000 lb of chemicals is used during a calendar year.

used in industrial process water treatment.

These ranges, too, can be exceeded on both the high and low sides, depending on the nature of the process, quality of water, climatic conditions, pretreatment, and the type of formulations employed.

Energy/environment dovetail

As seen in the three cases cited (see box), internal water preparations have been used principally to facilitate production processes—to avoid corrosion, scaling, fouling, and the like. This remains a key objective. But a second, major concern has been raised in the late 1960's and early 1970's; this was, of course, the environmental quality issue. This consideration further promoted the use of internal water preparations and has contributed to the shifting in the proportion of chemicals employed. The trend is toward utilizing nonchromate, nontoxic, and nonpolluting inhibitors in the case of cooling, just to cite one key example.

Finally, the third and most recent consideration is that of energy conservation. The presence of even small quantities of microorganisms can add drastically to fuel costs and the cost of operating heat exchangers, cooling towers, boilers, and so forth. Using internal water preparations can cut energy costs in a very dramatic way, while facilitating production and cleansing water and wastewater. It is indeed fortunate that environmental and energy considerations dovetail in the case of operating factories and commercial buildings.

Acknowledgment

The author acknowledges the kind assistance of several key chemical company executives who wish to remain anonymous. He is also grateful for the kind courtesy of The Whiston Group for supplying the data concerning the Chicago Civic Center.

Andrew C. Gross *is professor of marketing and international business at Cleveland State University where he has served on the faculty since 1968. He is also a consultant to and a member of the board of directors at Predicasts, Inc., a large marketing research and business information firm in Cleveland, Ohio. This article is based on a major monograph written for Predicasts, Inc. (Water Treatment Chemicals, 3rd ed.).*

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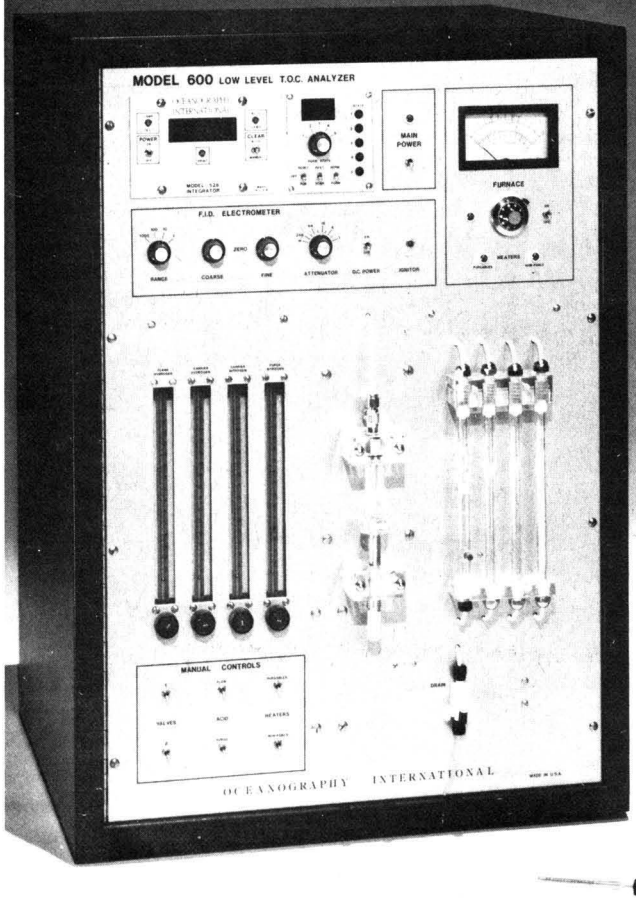

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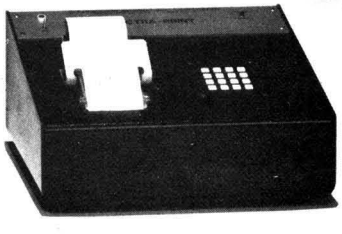

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CIRCLE 7 ON READER SERVICE CARD

The new Endangered Species Act

1978 amendments establish elaborate consultation and exemption procedures that require that biological information and human and economic factors be considered when resolving conflicts

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On October 2, 1978, a U.S. District Court determined that the Rural Electrification Administration and the Army Corps of Engineers had failed in their responsibilities under the Endangered Species Act of 1973 (PL 93-205 as amended by PL 94-32 and PL 94-359). As a result, the court gave a "stop work" order to the sponsors of the partially completed, $1.6 billion Missouri Basin Power Project—a coal-fired power plant slated to provide power to more than a million people in eight midwestern states.

The decision, which resulted in part from the potentially adverse effects of consumptive water use on the whooping crane's critical habitat 275 mi downstream, underscored heated debate in Congress on proposed amendments to the Act. The Missouri Basin Project and the Tellico Dam Project, which also made newspaper headlines, were apparent examples of irresolvable conflicts between proposed developments and the Act's requirement that federal agencies protect threatened and endangered species and their critical habitats. Congress was struggling with the question, Under what circumstances does the need to complete a federal development action outweigh the need to protect and preserve endangered species?

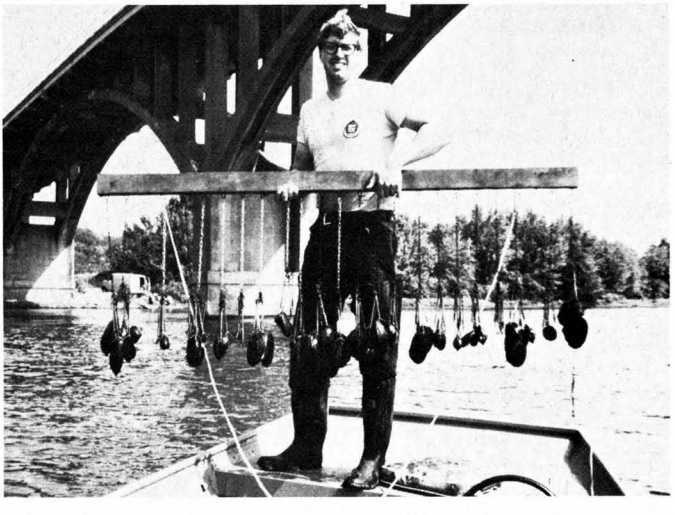
A new provision

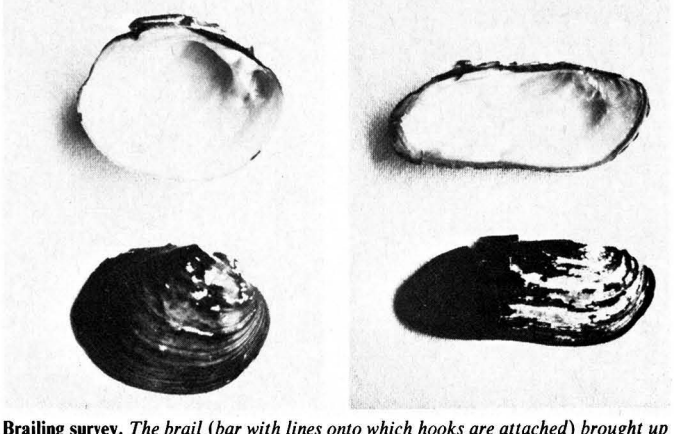
Congress specifically addressed Section 7 of the 1973 Act, which states that all federal agencies must ensure that actions authorized, funded, or carried out by them do not jeopardize the continued existence of endangered or threatened species or result in the destruction or modification of critical habitats. In the past, only biological data could be considered in solving conflicts between proposed actions and the Section 7 mandate.

The congressional debate centered on how to broaden the Act to allow consideration of human and economic as well as biological information in resolving conflicts. The amendment, passed in the closing hours of the last congressional session, provides the latitude for considering these other factors by allowing exemptions to be granted in certain instances, even if the action will harm an endangered species or critical habitat area.

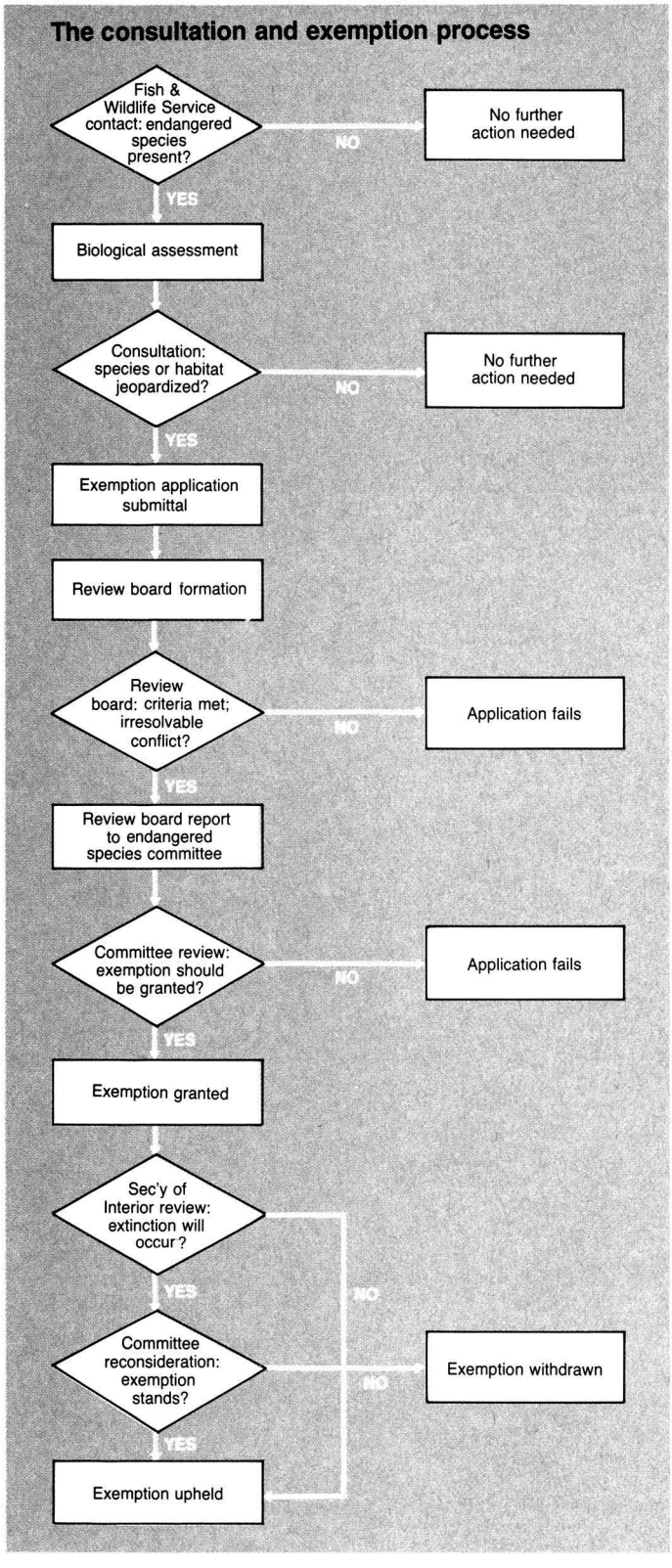
Under the revised Section 7 in the Endangered Species Act Amendments of 1978 (PL 95-362), exemptions may

Whooping crane. *An accommodation between this endangered bird and the Missouri Basin Power Project was achieved, and the Project was granted an exemption under the Act*





Brailing survey. *The brail (bar with lines onto which hooks are attached) brought up the endangered Higgins' Eye mussel (left) and Spectacle Case mussel (right) during a biological assessment of the upper Mississippi River*



be granted in three ways. The President may grant an exemption for declared major disaster areas. The Secretary of Defense can exempt actions if he finds them necessary for national defense. And, finally, the newly created seven-member Endangered Species Committee may exempt actions if there are no reasonable and prudent alternatives; if the benefits of the action clearly outweigh alternatives consistent with conserving the species; if the action is in the public interest; and if the action is of regional or national significance.

The exemption process

The amendments included special provisions for the Tellico Dam Project and the Missouri Basin Power Project: the Endangered Species Committee was required to consider granting exemptions to them within 90 days after enactment. In January 1979, the Committee denied the Tellico Dam Project an exemption from the Act because its economic benefits did not clearly outweigh the costs. At the same time, an exemption was granted the Missouri Basin Power Project because of an agreement by its sponsors to provide an irrevocable trust fund of $7.5 million to be used for maintenance of the whooping crane habitat.

The Tellico and Missouri Basin Power Projects received special consideration because of the immediate need to resolve costly conflicts. However, all future decisions on exemption will come through a detailed consultation and review process that could take more than 2 years to complete.

As shown in the accompanying flow chart, the first stage in the exemption process is the completion of a biological assessment. This new requirement affects all construction projects after November 10, 1978, the date of enactment of the new Act. For each new project, federal agencies must contact the U.S. Fish and Wildlife Service and request information on whether any threatened or endangered species are present in the project area. If such species are present, the agency must, within 180 days, complete a biological assessment to identify any that are likely to be affected by the action.

After completing the biological assessment, the agency must initiate a consultation process with the U.S. Fish and Wildlife Service. Within 90 days after initiation, the Fish and Wildlife Service must consider the results of the biological assessment and other pertinent information and publish an opinion as to whether or not the action would jeopardize the existence of a listed species, or negatively modify a

critical habitat. The opinion must detail how the agency action affects the species or habitat and must suggest reasonable and prudent alternatives that would prevent adverse effects.

If the opinion states that the species or critical habitat will be placed in jeopardy, the project cannot continue as planned unless an exemption is granted. The agency, the governor of the state in which the action was to occur, or the permit or license applicant may submit, within 90 days, an application for exemption from the Act's protective requirements. Proposed regulations for the exemption process were published in the February 7, 1979 *Federal Register*.

Upon receipt of the application, a review board is formed to consider the applicant's eligibility for exemption. The three-member panel (comprised of one member appointed by the Secretary of the Interior; one member appointed by the President to represent the affected state; and an Administrative Law Judge selected by the Civil Service Commission) must determine, within 60 days of formation, if an irresolvable conflict exists between the proposed action and the requirements of Section 7. The review board must further determine that the applicant:

- carried out its consultation responsibilities in good faith
- made a reasonable and responsible effort to develop modifications or alternatives that would avoid the adverse impacts
- conducted a biological assessment as required
- refrained from making an irreversible or irretrievable commitment of resources that would foreclose the formulation or implementation of any reasonable and prudent alternative measures.

Violation of any of these criteria disqualifies the application from possible exemption.

When the review board determines that an applicant for exemption has met the criteria listed above, it must prepare a report within 180 days for submittal to the Endangered Species Committee. The report must address the availability of alternatives to the agency action; the nature and extent of the benefits of the agency action; the evidence concerning whether or not the action is of regional or national significance and is in the public interest; and the availability of mitigation or enhancement measures that could be required by the Committee to lessen the adverse effects of this action.

Once the review board report is submitted to the Endangered Species Committee, 90 days are allowed for the Committee to make a final determination. The Committee, after considering the criteria, must decide either to deny the application or grant an exemption. If an exemption is granted, the Committee must specify such mitigation and enhancement measures as transplantation and habitat improvement that must be taken to minimize the adverse effects on the species. In the Missouri Basin Power Project decision, for example, the Committee accepted the recommendation of the applicant and other interested parties that a trust fund be established for use in habitat maintenance.

The Committee's decision to grant an exemption may be subject to three additional reviews. First, the Secretary of the Interior reviews the decision and may determine that the action would result in the extinction of the species. If so, the Committee then has 30 days to reconsider the exemption. Second, the Secretary of State determines if the exemption conflicts with the terms of any international agreements. Finally, all decisions of the Endangered Species Committee are subject to judicial review in the U.S. Court of Appeals.

Endangered Species Committee Members

Secretary, Dept. of the Interior, chairman
Secretary, Dept. of the Army
Secretary, Dept. of Agriculture
Administrator, EPA
Administrator, NOAA
Chairman, Council of Economic Advisors
State representative[a]

[a] Appointed by the President

New requirements' implications

Despite the fears of some environmental groups that the Endangered Species Act Amendments of 1978 weakened existing legislation, endangered species considerations will not become any less important in the future. More than 200 plant and animal species are currently classified as either threatened or endangered in the U.S. These species represent a variety of life forms—from plants such as the Furbish lousewort, to fishes such as the snail darter, to a crustacean, the Socorro isopod.

Furthermore, the survival requirements of threatened and endangered species encompass a variety of habitats and geographic regions. Endangered species legislation affects all geographic areas of the country and its territories. The Act's explicit statement of applicability to all actions "authorized, funded, or carried out" by a federal agency further emphasizes the fact that the presence, distribution, and survival requirements of threatened and endangered plants and animals will continue to be important considerations in planning and implementation of most major developments.

By including provisions for exempting actions from the Section 7 requirements, Congress expressed the belief that there are circumstances in which the preservation of endangered species must be secondary in importance to human and economic considerations. The exemption granted the Missouri Basin Power Project is the first example of such circumstances, and it is probable that there will be future federally authorized actions that cannot be developed in a manner that avoids a conflict with a listed species.

However, the requirements of the consultation and exemption processes imply that many or most conflicts can be resolved during consultation. In particular, the provision prohibiting the irreversible and irretrievable commitment of resources by the developer during consultation and the provision requiring the opinion to suggest "reasonable and prudent alternatives" to actions that jeopardize a species emphasize a cooperative planning process involving the developer, the U.S. Fish and Wildlife Service, and other federal agencies.

If threatened and endangered species are considered early in the planning process, it is usually possible to design the project so that the species or their habitats are not harmed. Needed siting or design modifications are not so costly if identified early in the planning process and may be far less expensive than the costs associated with irresolvable conflicts and the time required to complete the new exemption process.

Thomas Shoemaker *is a terrestrial biologist at ERT's facilities in Fort Collins, Colo. He has worked on several projects where endangered species were of special concern and has experience with bald eagles, whooping cranes, and peregrine falcons.* Coordinated by LRE

Do man-made sources affect the sulfur cycle of northeastern states?

Profoundly. And the impact is most readily seen in the atmosphere where man-made emissions exceed natural sources by a factor of five and spill over into the environment to create high levels of sulfate in rain, soils, and bodies of freshwater

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Scott Lynn
University of California, Berkeley
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Atmospheric problems associated with the release of large quantities of sulfur-dioxide (SO_2) have been the subject of concern in recent years. A costly control policy has resulted from EPA studies dealing with the health and welfare implications of high concentrations of SO_2 and sulfate (SO_4) particles. Increased dependence on coal may aggravate sulfur pollution in the future as lower-sulfur-content petroleum fuels dwindle.

Through the work of several investigators, the major fluxes of sulfur compounds through the global environment have been identified (Figure 1). The atmosphere receives volatile sulfur from soil bacteria and releases sulfur through wet-and-dry deposition processes. The deposited compounds join with fertilizer and eroded mineral sulfur in the soil. Leaching by groundwater carries the soil sulfur to rivers and finally to the oceans (where deposition regenerates sulfur-containing rocks). Estimated volatile sulfur production from bacteria outweighs man-made sulfur sources by roughly 50%, indicating a relatively small impact globally for the latter.

The major impact of SO_2 appears to be on a regional rather than a global scale. Approximately one-sixth of all anthropogenic sulfur emitted in 1975 was released over 0.6% of the global land area in the northeast U.S. By collecting and evaluating available data on sulfur fluxes in this area, an assessment of man's impact on a regional basis may be made.

Figure 2 outlines the region of the northeast U.S. referred to in this article as the "study region." Characterized by high SO_2 emissions, the region has been the subject of EPA and EPRI (Electric Power Research Institute) studies on the effects of high levels of atmospheric sulfates, particles transformed over time from SO_2. The data presented here reflect the situation of the early 1970's.

TABLE 1
Early 1976 SO_2 emissions[a]

State	Emissions in study region (10^6 tons/y)	Emission density (tons/(mi^2·y))
Mass.	0.65	82.33
R.I.	0.05	45.37
Conn.	0.24	49.30
N.J.	0.73	97.12
Del.	0.27	134.09
Md.	0.51	51.89
Pa.	4.51	100.10
Va.	0.86	21.62
W.Va.	0.54	22.23
Ky.	2.44	60.84
Ohio	5.82	141.57
Ind.	3.25	89.82
N.Y.[a]	1.62	60.11
Mich.[a]	1.67	107.52
Ill.[a]	2.51	70.67
	25.67 × 10^6 Total tons of SO_4/y	76.02 Wtd av

[a] As 10^6 tons of SO_4/y.
[b] Only emissions for the portion of the state within the study region were used.
Source: EPA's NEDS

Emissions, deposition, transportation

Emissions data for the study region were taken from EPA's National Emission Data System (NEDS) data bank. The average emission density of the 340 000-mi^2 area is 76 tons of SO_4/(mi^2·y) [equivalent to 51 tons of SO_2/(mi^2·y) or 25 tons of S/(mi^2·y)]. This compares to a global average of about 3 tons of SO_4/(mi^2·y). About two-thirds of these emissions are produced by utilities, mostly via coal combustion. As seen in Table 1, emission densities are highest in Ohio and Delaware with 142 and 134 tons of SO_4/(mi^2·y), respectively. Total emissions are approximately 26 × 10^6 tons of SO_4/y.

Once airborne, SO_2 may be oxidized to sulfate particles, transported, or deposited.

Several oxidation mechanisms are possible: direct photooxidation; various forms of indirect photooxidation; and catalyzed oxidation on liquid droplets or dry surfaces. The rate of oxidation and type of sulfate produced in a particular area are functions of the availability of various catalysts (such as heavy metal ions or particle carbon) or

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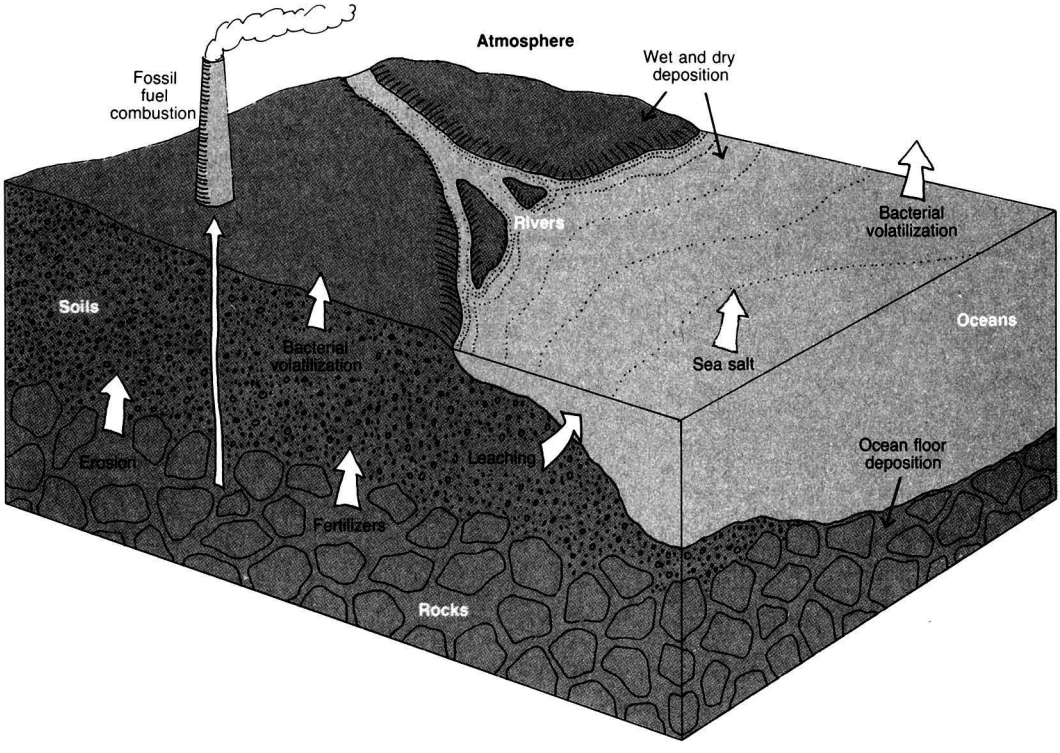
FIGURE 1
Major components of the global sulfur cycle



oxidants (NO_x and $OH^{\cdot}$). Oxidation rates from 1–20%/h have been reported in plume studies.

These secondary sulfate particles formed from SO_2 lie in the 0.1–1 μm size range, the so-called "accumulation mode." The ability of particles in this size range to penetrate deeply into the lungs has created concern about the health effects of sulfates, which appear to be functions of cation type. Other problems associated with sulfate particulate matter are its slow deposition rate, which makes prospects of long-range sulfur transport worse, and its ability to scatter light, causing visibility reduction. Further research on the atmospheric sulfates is being conducted, and the EPA expects to decide on a control policy by the early 1980's.

Sulfur is removed from the atmosphere by wet and dry deposition. Data on wet deposition by rainwater analyses are sparse, but the results of a few studies indicate that approximately 5 $\times$ 10^6 tons of SO_4/y is removed by rain in the study region (Table 2). This average of 15 tons of $SO_4/(mi^2 \cdot y)$ far exceeds the global land average [less than 5 tons of $SO_4/(mi^2 \cdot y)$].

Dry deposition is estimated through the use of deposition velocities. This quantity is an effective mass-transfer coefficient that relates deposition rate to ground-level concentrations (see eq 1).

The range of experimentally measured deposition velocities for SO_2 is 0.5–2.5 cm/s and from 0.1–1 cm/s for SO_4 particles. The actual deposition velocity is a function of various meteorological conditions as well as the character of the ground surface. For the purposes of this article, values of 1 cm/s for SO_2 and 0.25 cm/s for SO_4 were chosen.

Average SO_2 and SO_4 concentrations in the study region were taken from 24-h samples collected by federal, state, and private agencies. Five years of data for the early 1970's was reviewed, and a rough contour map of pollution concentration was produced from the data. Average sulfur concentrations in the region are about 16 $\mu g/m^3$ SO_2 and 12 $\mu g/m^3$ SO_4. From eq 1, total deposition for the study region is about 8 $\times$ 10^6 tons of SO_4/y, with SO_2 responsible for 90% of the total.

Estimating the transport of sulfur in the atmosphere will require use of a simplistic model of the troposphere. This model divides the troposphere into two layers: the region closest to the earth—the mixing layer—where unstable air causes vigorous vertical mixing to create a relatively homogeneous zone; and the more stable area above, where vertical mixing is less apparent and concentration gradients develop (especially for pollutants with short atmospheric residence times). Ground-level deposition processes reduce the residence time of pollutants in the mixing layer, whereas pollutants reaching the upper layer are more susceptible to horizontal transport.

By using wind velocity, average mixing height, and pollutant concentration data for National Weather Service stations located around the perimeter of the study region, the net transport of a pollutant through the mixing height can be calculated. The first step in this calculation is an estimate of the air influx rate within the mixing layer for each border site (see eq 2). The air influx rate is combined with pollution concentration data at the border sites to produce a plot of concentration air influx rate [μg of $SO_4/(m \cdot s)$] vs. border location. The area under this plot is the pollutant influx rate through the mixing layer.

Performing this analysis for the study region reveals a net efflux of SO_2 (1.1 $\times$ 10^6 tons of SO_2/y equivalent to

Basic equations of the sulfur cycle

Dry deposition

$$R_d = v_d c_\infty A_g \quad (1)$$

where
- R_d = deposition rate (μg/s)
- v_d = deposition velocity (m/s)
- c_∞ = ambient concentration (μg/m^3)
- A_g = ground area (m^2)

Air influx across a border

$$\alpha = \mu_{g,in}(\bar{s}_h/\bar{s}_g)\bar{H} \quad (2)$$

where
- α = air influx rate through the mixing layer (m^2/s)
- $\mu_{g,in}$ = cross-border component of the resultant wind velocity vector (m/s)
- $\bar{s}_h$ = average wind speed through the mixing height
- $\bar{s}_g$ = average ground level wind speed
- $\bar{H}$ = average mixing height

River effluxes

$$D = \left(\sum_i A_i \sum_j \left[\left(c_{ij}d_{ij} \Big/ \sum_j d_{ij}\right)\right]\right)\left(k_w W A_t \Big/ \sum_i A_i\right) \quad (3)$$

where
- D = total sulfate discharge of rivers in the study region (tons/y)
- c_{ij} = sulfate concentration of river i, sample j
- d_{ij} = discharge of river i, sample j
- A_i = drainage area of river i
- W = total rainfall in the study region
- k_w = fraction of rainfall which enters rivers
- A_t = total area in study region

Overall cycle balances

$$\text{atmosphere: EM} + B = \text{DD} + \text{WD} + \text{NPE} \quad (4)$$

$$\text{soil: } F + \text{ER} + I + \text{DD} + \text{WD} = R + B \quad (5)$$

where
- B = bacteriogenic flux
- DD = dry deposition (8 × 10^6 tons of SO_4/y)
- EM = anthropogenic emissions (25 × 10^6 tons/y)
- ER = erosion and acid mine drainage (3 × 10^6 tons/y)
- F = fertilizer additions (1 × 10^6 tons/y)
- I = industrial sulfate flux to soil (0.5 × 10^6 tons/y)
- NPE = total net pollutant efflux from atmosphere
- R = river efflux (15 × 10^6 tons/y)
- WD = wet deposition (5 × 10^6 tons/y)

Partial global fluxes

$$F_{sr} = F_{gl}(A_{sr}/A_{gl}) \quad (6)$$

where
- F_{sr} = study region flux
- F_{gl} = global land flux
- A_{sr} = surface area of study region
- A_{gl} = global land surface area

1.7 × 10^6 tons/y of SO_4) and SO_4 (0.8 × 10^6 tons of SO_4/y). Slight influxes through the southern and western borders are outweighed by large effluxes from New Jersey, New York, and the New England states.

The total pollutant flux may be calculated from a balance of the atmospheric portion of the regional cycle and includes the transport above the mixing height. An estimate of other sources of atmospheric sulfur will be necessary before completing the cycle.

Ground-level fluxes

Fertilizers, erosion, acid mine drainage, and sulfate sludge-pond drainage all contribute to the soil-sulfur load.

Data on supplemental sulfate applications were supplied by the Sulphur Institute (Washington, D.C.). Approximately 1 × 10^6 tons of SO_4/y is applied in the study region. It is interesting to note that soils in the study region, particularly in New England, rarely suffer from lack of sulfur, possibly because of the preponderance of atmospheric sulfur (Table 2).

Natural erosion may be evaluated from denudation rates of bedrock in the study region. Mechanical denudation (primarily a function of land elevation) is estimated at 80 tons of rock/(mi^2·y). Chemical denudation (primarily a function of rock type, extent of watering, and vegetation) is estimated at 100 tons of rock/(mi^2·y). Combining these denudation rates with data on rock types and their SO_4 contents, natural erosion in the study region is estimated at between 0.3 and 0.7 × 10^6 tons of SO_4/y.

Mining operations have a very large impact on SO_4 production via erosion processes. The Department of Interior estimates 2 × 10^6 tons of SO_4/y escape mines in Appalachia alone as acid drainage (75% of which is from deep mines).

Excessive erosion around mine-spoil piles (mainly from surface mining) generates additional sulfate. An estimated 2200 mi^2 (or 0.7%) of the study region has been disturbed by strip mining. A long-term study of the effects of strip mining in Beaver Creek Basin, Ky., concluded that a 25-fold increase in erosion was caused by stripping 10% of the land. We would, therefore, expect approximately two times the natural erosion to occur in the study region as a result of 0.7% strip mining. These additions increase the erosion flux to approximately 1 × 10^6 tons of SO_4/y, or the total SO_4 derived from rocks to 3 × 10^6 tons/y (Table 3).

Various industrial processes consume large amounts of sulfur each year, mainly as H_2SO_4; the major user is phosphate fertilizer manufacturing. Some sulfur ends up in the atmosphere, but by far the major part of industrial sulfur ends up in 12×10^6 tons of SO_4/y of sulfate sludge. Scrubber operations add an additional 10^6 tons of SO_4/y to the sludge pool. Reviews of sulfate overflow from sludge ponds show that less than 1% of the sulfate escapes as pond overflow. Certainly, additional sulfate escapes as seepage to groundwater, but it seems unlikely that the total amounts to more than 5% of the total deposited sludge ($<0.5 \times 10^6$ tons of SO_4/y).

Soil–sulfur reactions, river removal

As seen in Figure 3, sulfur compounds in the soil may undergo a wide variety of reactions. Maintaining a proper level of sulfur for plant nutrition is dependent on many of these reactions for both conversion of sulfur to utilizable form and conversion of soluble SO_4 to a form less readily leached by rainwater. Typically, 90% of the soil sulfur in humid regions is organic. Aerobic soils generally contain much less sulfur than anaerobic soil, possibly because the action of sulfate-reducing bacteria produces H_2S, which precipitates as FeS in the presence of iron.

Two mechanisms remove sulfur from the soil. First, soluble sulfates are leached from the soil by rainwater and are eventually carried to the seas in the rivers. Second, soil bacteria volatilize sulfur through metabolism of sulfur-containing amino acids and the reduction of sulfate to sulfur. Early studies of the sulfur cycle assumed that H_2S production by anaerobic, sulfate-reducing bacteria (such as *Desulfovibrio desulfuricans*) was the major biogenic source. Recent evidence, however, suggests that compounds such as dimethyl sulfide, dimethyl disulfide, and methyl mercaptan may be of greater importance and that aerobic soils may be equal contributors.

No major field studies of sulfur volatilization are reported. Laboratory volatilizations are suspect owing to the inability of small lab samples to include leaching and reactions occurring in the soil; they may also be subject to bacterial inhibition by sulfide accumulation. How much, what compounds, and when and where volatile sulfur is produced remain major uncertainties. Further research in these areas is certainly warranted.

Equation 3 is the formula by which sulfate efflux in rivers was estimated. Discharge-weighted averages must be

TABLE 2

Deposition of sulfate in rainwater and fertilizer applications

State	Sulfate in rainfall: tons/(mi^2-y)	Sulfate in rainfall: 10^3 tons/y	Fertilizer applications[a] (10^3 tons/y)
Mass.	10.3	81	5.7
R.I.	8.6	9	1.2
Conn.	10.8	53	4.6
N.J.	17.4	131	14.9
Del.	12.8	25	9.5
Md.	12.3	121	27.4
Pa.	13.4	604	68.1
Va.	8.6	341	72.3
W.Va.	10.8	261	5.5
Ky.	12.1	486	60.3
Ohio	14.0	574	138.0
Ind.	17.4	630	151.2
N.Y.[b]	12.1	326	33.8
Mich.[b]	14.3	220	25.8
Ill.[b]	17.4	619	107.2
	Av 13.3	Total 4481	Total 725.0

[a] Extrapolated from data supplied by the Sulphur Institute. [b] Data given for portion of state within study region.

TABLE 3

Ground-level fluxes of soluble sulfate to the soil and groundwater[a]

	Total sludge	Overflow	Seepage	Deposited sludge
Sulfate sludge				
Industry	12.0	0.3	0.03??	11.94
Scrubbing[b]	1.0	0.003	0.003??	1.0
Total	13.0	0.033	???	12.94
		Total assumed $\ll 0.5$		
Other sources				
Normal erosion				0.5
Excess erosion (from strip mining)				0.5
Acid-mine drainage				2.0[c]
Total				3.0

[a] Expressed as 10^6 tons of SO_4/y. [b] Figure for early 1975, should rise rapidly through the 1980's as more flue-gas desulfurization units come on line. [c] U.S. Department of Interior estimate.

TABLE 4

Comparison of global land sulfur cycle with the sulfur cycle of northeast U.S.[a]

Cycle flux	Global	Study region (northeast U.S.)[b]: By land-area fraction	Study region (northeast U.S.)[b]: Est by data
SO_2 emissions	150	0.88	25.0
Bacteriogenic prodn.	210	1.23	2.0
Precip. + dry depos.	360	2.11	13.0
Fertilizer	33	0.19	1.0
Weathering	42	0.25	1.0
Acid-mine draining	?	?	2.0
Industrial operation	?	?	0.0
Stream load	225	1.32	15.0
Atmos transport out	0	0.00	10.0

[a] 10^6 tons of equivalent SO_4/y. [b] Figures given as "by land area fraction" are calculated by using the global flux, multiplying by the study region land area, and dividing by the global land area. Figures listed as "est by data" are the actual fluxes as estimated from the data presented in this report.

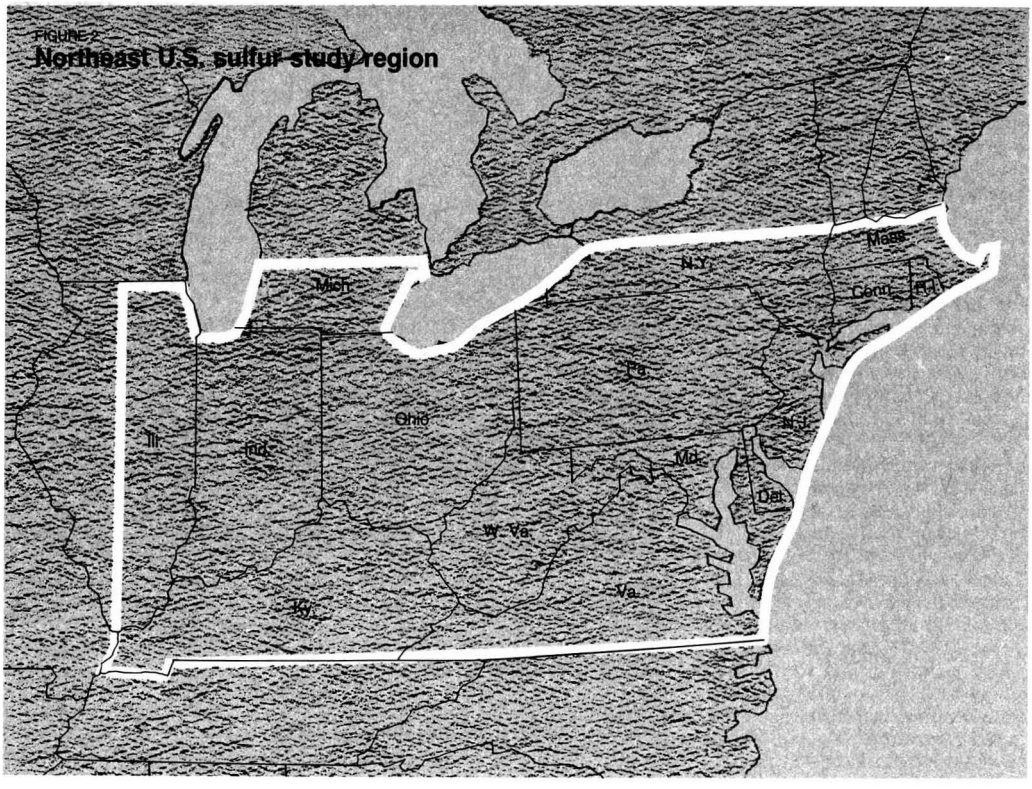
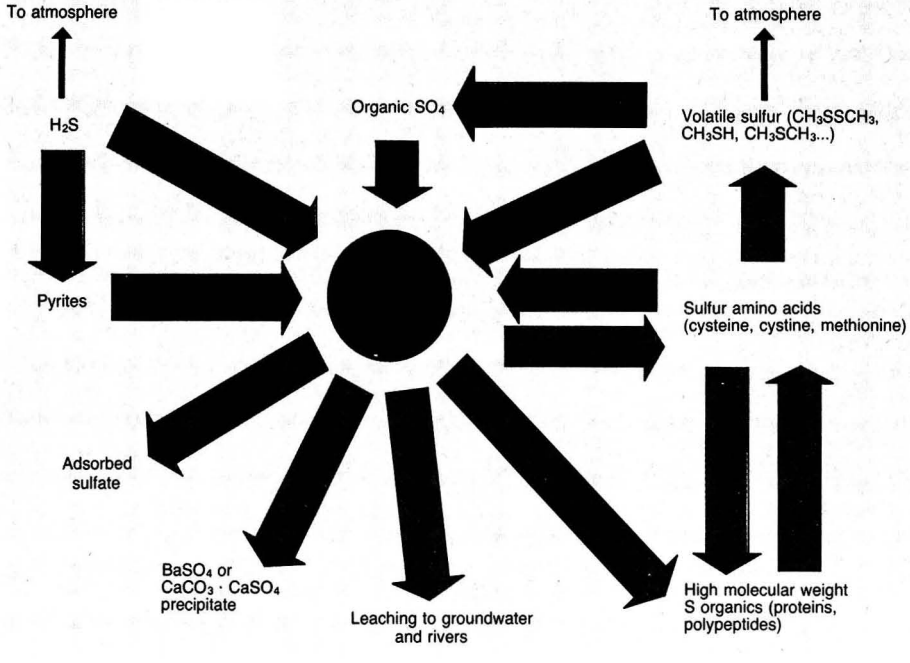


FIGURE 2
Northeast U.S. sulfur study region

FIGURE 3
Soil sulfur chemistry



used to eliminate the effect of higher concentrations during periods of low flow, and care must be taken to choose sampling sites that are free from tidal effects. Grab samples of river water, analyzed by the U.S. Geological Survey for major rivers, serve as a data source for discharge and concentration data for eq 3. The total sulfate discharge in rivers in the study region is approximately 15×10^6 tons/y.

Cycle balance

Total atmospheric transport and the biogenic flux may be calculated by balancing the soil and atmospheric portions of the cycle. Assuming no atmospheric or soil-sulfur accumulation, the balance reduces to eq 4 and 5. From these equations, the bacteriogenic flux is calculated at 2×10^6 tons/y. This figure is a result of differences of much larger terms and could easily be inaccurate by a factor of 2 or 3. We conclude that this flux is likely to be between $1\text{-}5 \times 10^6$ tons of SO_4/y.

The net pollutant efflux from the atmosphere (14×10^6 tons of SO_4/y) may be checked by calculation of the concentration in the mixing height necessary to create such an efflux. The net addition of sulfate to the mixing height in the study region is $25 + 2 - 14 = 13 \times 10^6$ tons/y. Using an average mixing height of about 1000 m and an average residence time of 1 day in the mixing layer yields an average sulfate concentration of 37 $\mu g/m^3$. This figure agrees well with the figure of 36 $\mu g/m^3$ that results from addition of SO_2 and SO_4 contributions to the concentration data.

Summing up

Table 4 provides a comparison of the fluxes for the study region to the fluxes that would be calculated from the global land sulfur cycles by using eq 6. There are several inferences which may be drawn from this regional cycle. First, in regions of high mining activity, acid drainage and erosion of mining spoils may overshadow the natural fluxes of eroded sulfate. In combination with atmospheric excess, the erosion leads to excessively high sulfate concentrations in rivers and streams.

Atmospheric effects are most pronounced. Anthropogenic sources exceed biogenic sources by a factor of about 10. The health and welfare implications of such widespread disruption of the natural ecosystem have only begun to be investigated, and a great deal of debate surrounds the control issue. Preliminary indications are that it will be important to consider the physical and chemical state of the sulfur in examining its health effects.

The net total efflux from the atmosphere (14×10^6 tons/y) is considerably larger than the efflux through the mixing layer calculated earlier (2.5×10^6 tons of SO_4/y). Although there is considerable room for error in these approximations, this implies that a large portion of the SO_2 leaves the lower layer of the atmosphere (where deposition predominates) and enters the region where long-range transport becomes likely. For the northeast U.S., this is advantageous, as transport will bring the pollutant over oceans for later deposition. The environmental impact of long-range transport for a region such as northern Europe, however, could be considerably more deleterious.

The regional atmospheric efflux is likely to be a product of man's activity. Biogenic volatile sulfur is produced at ground level where deposition may be rapid. Elevated emissions from smokestacks tend to isolate the sulfur compounds from deposition. Primary natural sulfate particles (from sea salt and dust) are much larger in size than the easily transported secondary particulates and have correspondingly more rapid deposition rates. Secondary sulfate particles are less likely to be formed in a natural environment relatively free of oxidants and oxidation catalysts. It is likely that the net efflux in an undisturbed ecosystem is negligible when compared to the efflux in a region of such high man-made sources.

The supply of sulfur to the soil is greatly enhanced by atmospheric excesses. The overloading of the soil may also enhance bacteriogenic volatilization. This type of land-air interaction may allow further transport of pollutant sulfur in a progressing cycle of deposition, volatilization, and redeposition. Enhanced biogenic production may also be an important factor in creating seasonal variations in sulfate concentrations occurring throughout the Northeast.

Previous studies of sulfur cycles have generally assumed no soil-sulfur accumulation. In a region of ubiquitous sulfur, however, this assumption may not be valid. The most likely site of accumulation would be in anaerobic soils with ample supplies of fresh organic matter (to feed sulfate-reducing bacteria) and iron (to precipitate FeS or FeS_2).

The future

Based on implementation of a stringent control policy, EPA estimates show a very slow increase in SO_2 emissions over the next 10 years. Power consumption, however, is expected to continue to rise.

Current political tendencies seem to favor increased exploitation of coal, which will be a strain on sulfur loading in two ways: increased acid-mine drainage and more power-plant emissions. Emissions control will undoubtedly produce more sulfate sludge. The potential environmental effects of this ever-growing pile of sludge should be further investigated, including studies of drainage and volatilization from sludge ponds. Conversion of sludge to a nonporous, nonreactive form and disposal in environmentally isolated regions seem desirable as a means of limiting its potential impact.

Additional reading[a]

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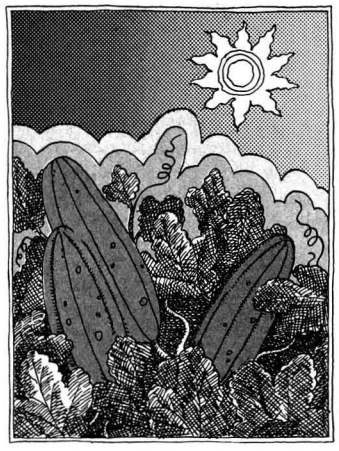

Sunshine out of cucumbers, an energy perspective

This plenary address was given at the International Materials Congress sponsored by the National Academy of Sciences and the National Academy of Engineering, held in Reston, Virginia, on March 26–29, 1979

Lord Ritchie-Calder
Edinburgh, Scotland

Those of you who know more about Gulliver's Travels than Walt Disney's version of them may recall his visit to the Grand Academy of Lagado and his encounter with one of the fellows. I quote his account, as reported by Jonathan Swift:

"He had been eight years upon a project for extracting sunbeams out of cucumbers, which were to be put in vials, hermetically sealed, and let out to warm the air in inclement summers. He told me, he did not doubt that in eight years more he would be able to supply the governor's gardens with sunshine at a reasonable rate, but he complained that his stock was low and retreated me to give him something as an encouragement to ingenuity, especially since this had been a very dear season for cucumbers. I made him a small present, for my lord had furnished me with money on purpose because he knew their practice of begging from all who go to see them."

That was written 250 years ago as Swift's satire on the Royal Society of London (or so it is alleged), but you may agree that it has a familiar ring of present day grant applications: an ongoing energy project; the long leadtime of R & D ("just eight years more") on top of the eight years feasibility study; and the effects of inflation on research materials.

Maybe, in the present energy crisis, we should look again at the possibility of extracting sunbeams out of cucumbers . . . if we could get enough cucumbers.

Cucumbers explained

The cucumbers are what we are here to discuss. Let us, with the arrogance of *Homo faber,* postulate that human integrity can artefact anything provided that the energy and the basic elements are available and if we have got our priorities right. I remember an occasion when Alvin Weinberg, questioned on the availability of uranium, said, "If it comes to the bit we could burn rocks." On another occasion, Harrison Brown, contemplating (certainly with distaste) a possible world population of 50 000 000 000, said, "Then they will be eating rocks."

As I understood them, they were saying that we could extract the 10^{14} tons of uranium in the lithosphere or that we could recover the basic organic elements and make all the molecules of carbohydrates and amino acids and proteins. (We can recall that the Germans did rather well on ersatz margarine from the carboniferous deposits, and in November 1944 Albert Speer was lamenting to Hitler that the margarine factories had closed down because of the bombing of the coal mines of the Ruhr.)

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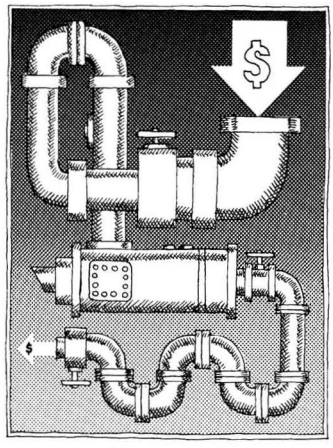


As in the case of cucumbers, much depends on the availability of the starting materials. Thirty years ago, the first acrylic fibre was produced by Du Pont. In Britain, a brash copywriter described it as "wool from peanuts." This was ill-advised and decidedly tactless because there happened to be a glut of wool and such a shortage of peanuts for oleomargarine that the British government was embarking on an expensive and ill-starred scheme to mass-produce peanuts in Tanganyika. I asked whether it would not be better to produce peanuts out of wool. On another occasion, a newspaper editor asked me with some excitement whether I had heard of a process for making milk out of grass. I said, "Yes, it is called a cow." He was, in fact, talking about leaf protein.

We put a price tag on a conversion process, but, of course, the unit cost ought to be expressed not in terms of money but of energy. In the case of cucumbers, one would have to reckon whether the bottled sunbeams would justify the energy consumed by the Fellow of the Grand Academy in the 16 years of feasibility study and R & D and, in the cropping of cucumbers, how much energy would go into the manufacture of artificial fertilisers, pesticides, weed killers, and the pumping of irrigation water.

Wartime

Energy expenditure itself is relative to need. The bookkeeping becomes unimportant, for example, in wartime. At the present time, in response to the oil shortage, interest in oil from coal has been vigorously revived, and the several processes are being subjected to cost-benefit analyses. Judging by the current literature on this subject, it might almost seem that we were starting de novo.

It seems to be forgotten that Friedrich Bergius got the Nobel Prize for the work he had started in 1914, converting coal dust into gasoline and lubricating oils. The Fischer–Tropsch reaction was developed to convert coal gas to hydrocarbons and synthesise petroleum-like substances. In a recent debate in the House of Lords, their Lordships had to be reminded, to their incredulous surprise, that, essentially, the German war machine in World War II ran on oil-from-coal processes. Hitler depended on them for most of his motor and aviation fuel and for ammonia for explosives. He did not launch his blitzkrieg until he could rely on his synthetic oil supplies. His only source of natural oil was the Romanian oil field, and the main objective of his attack on the USSR was to gain the possession of the Baku oil field.

At the peak of wartime production, Germany's oil-from-coal plants were supplying 6 000 000 metric tons per annum. The main centre was Leuna in the brown coal region of East Germany. The Germans failed in their thrust to the Caucasus. In May 1944, the American 15th Air Force wrecked the principal natural oil refineries at Ploesti in Romania. Simultaneously, the 8th U.S. Air Force attacked the synthetic oil plants in Germany. Albert Speer, Germany Armaments Minister, has written: "On May 4th 1944 the technological war was decided. With the attack of nine hundred and thirty-five daylight bombers of the American Eighth Air Force upon several fuel plants in central and eastern Germany, a new era in the air war began. It meant the end of German armaments production." For lack of oil from coal, the German tanks were to grind to a standstill in the Battle of the Bulge, and the German Air Force was to be grounded. But, for 6 years, the German war machine had been fueled from coal. To cost the project (and what a project!) would be meaningless, because one would be putting price tags on death and destruction, but what about energy-in and energy-out? And whatever happened to oil from coal in the intervening 30 years?

Oil from coal?

The answer to the latter is obvious: oil, apart from its intrinsic chemical values, was conveniently liquid and, in money terms, cheap. Its cheapness had scuppered Britain's well-advanced oil-from-coal program in the 1930's. Britain has been described as "a lump of coal entirely surrounded by fish."

We fueled the Industrial Revolution. We blackened our cities with millions of tons of soot from combustion that was less than 10% efficient. We still have an estimated 1.55×10^{10} tons in reserve. In the 1930's there was no premonition of North Sea oil, and we were entirely dependent on oil imports. It behooved us, therefore, to make the most of our coal. And in the 1930's we were proceeding to do so.

There were other compelling reasons. Britain then had a mining work force of over a million. In some of the mine fields the unemployment was over 80%, considerably because ships' bunker-coal, so hard to handle, was being replaced by oil. Work for miners was therefore a consideration.

Another reason was the belated recognition of the health hazards of coal. The notorious pea-soup fogs (the coal smogs) were thickening, and the sulphur from British chimney stacks was wafting northward to destroy the Scandinavian forests. There was a public health demand for smokeless fuel.

In the early 1930's, work on low-temperature carbonisation to produce smoke-free fuel for the domestic open fires was well advanced. It was reckoned that if the 120 million tons of coal being consumed in Britain were treated, they would yield, apart from smokeless fuel, 440 million gal of motor-spirit (nearly half of Britain's import requirements), 750 million gal of diesel oil, and 560 million gal of tar acids.

The process produced a rich gas. The approach here was the Fischer–Tropsch reaction. There was also the Bergius approach—pulverising the coal and pumping in hydrogen at high pressure and high temperature. The Imperial Chemical Industry, with a promise of Government tax protection, went ahead with a plant capable of producing 100 000 tons of petrol a year using 350 000 tons of coal (or half of 1 day's national production). The plant was to cost the equivalent of $10 million at the then exchange rate.

There were plans to salvage the depressed mining areas by establishing carbonisation plants and oil distilleries

at the pithead, establishing gas-grids, and erecting chemical plants and factories for plastics derived from coal.

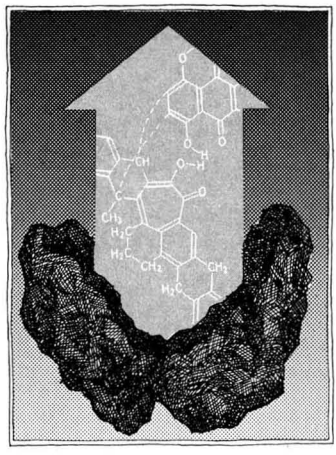
What went wrong with those rational ideas for oil from coal? Quite simply: in commercial terms, the availability of cheap oil. And that consideration persisted after the War, until OPEC served notice that oil would never again be cheap.

For the past 30 years, the chemical industry has moved its source of feedstock for bulk chemical production from coal to oil. In Britain, the work force in the mines declined to about a quarter of a million, and the consumption of coal declined from 5×10^{18} J/y in 1920 to 3×10^{18} at the present time. Solid fuel consumption has been dominated by blast-furnace coke for iron and steel. The chemical industry is the largest industrial consumer of primary energy, of gas and petroleum, and is second to the engineering and metal trades in the consumption of electricity.

Looking back

Thirty years ago, I went back to my home district in Scotland. Its industry was traditionally weaving—wool, linen, cotton, and, predominately, jute. One hundred and fifty years ago, still in the days of hand looms, an East Indiaman, under sail, had arrived in the Tay, on the East Coast of Scotland. It had on board a course fiber—jute. The cottage weavers could weave anything, so they produced a tough textile that could be used for sacking and baling and tarpaulin. Then they combined the linen trade and the jute backing, and jute also became the basis for carpets. With mass-production factories, the jute trade boomed. The jute was hauled 10 000 mi from Ganges Delta. Then the jute manufacturers of Dundee found that they could use cheap Indian labour and set up weaving plants on the Hoogly in competition with the Scottish production. And still the jute industry on the Tay boomed until the middle 1930's, when it began to suffer from the jute manufactured on the spot in India and what is now Bangladesh.

After the War, I suggested that Dundee should forget the long sea haul. Across the River Tay, in Fife, was a coal field. Why not take advantage of oil from coal and go over to man-made fibres? Today in my home



town there is a polypropylene plant working 24 h a day producing man-made fibres for the local weaving mills—but from oil, not coal. True, it will now come from the North Sea, but I still think that an opportunity of oil from coal was missed 30 years ago.

A second coming

It is coming in Britain. It is recognized that the oil and natural gas from the North Sea, so convenient to the British economy at the moment, will be depleted within 25 years, while the coal reserves can be reckoned in centuries. We talk about "the second coal era." It is current U.K. government policy not to approve any more oil- and gas-fired power stations. Environmental regulations will force the production of a clean low BTU coal gas to be piped to industry. The U.K. has a natural gas grid, but the British Gas Corporation is developing the technology that will provide methane synthesised from coal.

With the statutory imposition of smokeless zones, we are now in Britain and Europe beginning to clean up the soot-blackened buildings. In Edinburgh, which used to be called "Auld Reekie" because of its smoke pollution, and in London, which was already smothered by soot from "sea coal" in the 17th century, and in Paris, we can now have our architectural heritage, the stonework restored and flood-lit in all its pristine beauty.

We are not likely to tolerate the abuses of crudely burning coal as a fuel, especially since we can now treat coal as what it really is—a storehouse of essential chemicals. In it we have the feedstocks of the materials of the present and the future—pharmaceuticals, dyes and paints to brighten our lives, plastics, man-made fibres, even (it seems) fossilised antibiotics, single-cell protein fertilisers, herbicides, and pesticides.

Almost as a belated compensation for our past burden of soot, we have the carbon for carbon-fibres and their composites as structural materials. And, since we are committed to the internal combustion engine for a long time to come, we can have fluid hydrocarbons as well. With the development of MHD (magnetohydrodynamic) generators, it may be possible to get electricity directly from coal, instead of using it to generate steam for turbines. MHD is, of course, a major preoccupation of plasma physics with profound implications for fusion reactors. A very hot gas when in motion conducts an electric current. When it passes through a vertical magnetic field the ions are moved horizontally and can be collected by electrodes. Hence, if coal can be used to generate a very hot flame, electricity might be extracted.

Ongoing projects

Although there is a great deal of interest in the production of oil from coal, there are really only two centres of significant commercial production—in East Germany, the major scene of German wartime hydrogeneration activities, and South Africa. South Africa is entirely dependent for its natural oil on imports and, with recurring threats of sanctions, has reconciled itself to a siege economy.

As early as 1955 a plant to produce liquid hydrocarbons was brought into operation. It combined the Lurgi pressure gasification process with conversion through the Fischer-Tropsch process. In 1974 a new large plant was undertaken, sited in a coal field of 30 000 ha with sufficient coal for more than 60 years. The target was motor fuels (gasoline plus diesel oil) of the order of 1 500 000 tonnes/yr.

In Britain, the National Coal Board is developing two processes for converting coal to synthetic crude oil, with a special concern about aviation fuel. The present U.K. aviation kerosene requirements of 4 million tonnes per year is equivalent to 7 million tons of coal. However, aviation kerosene is not the only product, and energy is required to carry out the conversion. Estimates show that to meet present aviation requirements would mean liquefaction of 2.5 million tons of coal

a year, and the market is expected to double by 1995.

Synthetic oil

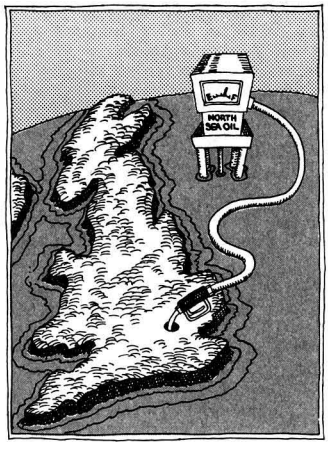
One process is liquid solvent extraction, in which coal is digested in an oil of high boiling point recycled from the process itself. The filtered coal solution is pumped to a hydrocracker where it is catalytically treated with hydrogen under pressure and converted into "syncrude" and hydrocarbon gases. The syncrude is distilled to separate light, middle, and heavy fractions. The light oil can be processed into transport fuels, chemicals, and plastics; the middle oil can be further hydrogenated to provide aviation fuel.

The heavy oil is recycled as a solvent for the early stages of the process or converted into coke. The other process is gas extraction, using the solvent power of gas at high pressure and temperature. When the coal is mixed with a suitable hydrocarbon gas, as much as 40% of the coal dissolves; the undissolved residue can be used to produce hydrogen or gaseous fuels. When the dissolved coal is transferred to another vessel at low pressure, the gas and the extract separate cleanly. The extract can be reacted with hydrogen to produce light oil, and the heavier fraction can be further processed to give aviation fuels.

Coal

I have laboured the point about coal because in addressing myself to materials and energy, I have been impressed (or depressed) by the way in which get-rich-quick considerations have diverted us from the effective use of our resources, of which coal is conspicuously one. Coal was a bit of rock that you burned very inefficiently in domestic grates and boiler furnaces. And as long as there was cheap muscle-energy in the form of badly paid miners, it did not matter.

In 1792, William Murdock first lit his house in Redruth, Corwall, with gas from coal but was derided as the "madman who is proposing to light London with smoke." Around the same time, Thomas Cochran, Earl of Dundonald (who, incidentally, as a volunteer admiral in the Chilean navy contributed to the defeat of the Spaniards and the liberation of Chile and Peru), invented a smokeless fuel process and explored the potentialities of coal tar.



From the coal tar, William Perkin of London, trying to make a synthetic quinine, discovered the first aniline dye, but it was left to the Germans with their greater regard for chemical engineering to exploit it and develop the dyestuff and pharmaceutical industry. Kerosene was manufactured from coal for lighting lamps in 1850 but within 10 years was overtaken by E. L. Drake's petroleum well. The internal combustion engine became a competitor with steam. The oil refineries as byproducts produced the feedstocks of the chemical industry, which might otherwise have come from coal or coal-tar distillation. And oil, until recently, was abundant and cheap.

The environmental concern

One salutary effect of the modern environment movement will be to remind us of the real cost. "The quality of life" is difficult to quantify, but we now take some notice of the "environmental impact," the social cost so long ignored. In industrial England in the 19th century the gloat was "where there is muck there is brass" (where there is filth there is money). The gracious countryside of the Midlands became "The Black Country." The Welsh living in the coal fields and working in the steel mills lamented "How green was my valley." The lowlands of Scotland became a blighted landscape of slag heaps, acid-poisoned lakes and streams, and industrial slums—the hallmark of prosperity. "Lancashire cough" was the chronic bronchitis of helpless millions. And so it was in the industrial areas of the U.S. and Europe. The present generation is now having to foot the bill for reclamation.

Concern with the environment is also reminding us that all life, and not just our livelihood, depends on energy and that energy derives from that fusion reactor, the sun. It is the sun which drives the weather machine, the winds, the waves, and the clouds that replenish our hydroelectricity. From it, through photosynthesis, we derive the food calories that sustain life and the coal and oil hydrocarbons.

More and more, we are turning to sun-derived organic materials, and when we achieve nuclear fusion as our source of energy, we will be imitating, on earth, the processes of the sun. When we are talking about the environment, our main concern is with the sun-created biosphere that sustains all life—the trees, the vegetation, the sea plankton, the food crops, the creatures, including Man himself. We exist because of sun-generated molecules.

In our awareness of environmental problems, we are being reminded of the wealth we are squandering because pollution is, in the final analysis, the discarding of unwanted products. Eutrophication, which is bedevilling our rivers, our lakes and seas, is just too many rich nutrients, from domestic wastes and industrial effluents, in the wrong place at the wrong time. Smoky chimney stacks and automobile exhausts are venting valuable chemicals. Noise pollution is squandered energy. British Aerospace Corporation has estimated that the engine-combustion system of a jet aircraft releases enough energy to heat 17 000 four-bedroom houses: That expresses itself in dB.

We mine and quarry the rocks of the lithosphere to extract metal, which we process and presently discard, with inadequate provision for recovery and recycling. Product manufacturers go for the end result and jettison as waste what they do not want. One recalls that the uranium for the first atom bombs came from the spoil heaps of Katanga, in the Congo. When radium was the premium product, Union Miniere had treated the uranium as waste. One also recalls that deep culture of penicillin became possible when it was recognized that corn-steep liquor, an embarrassing waste of the distilleries and starch manufacturers, was an admirable nutrient for the *Penicillium notatum* mould that secretes the antibiotic.

I once made a film for I.C.I. on en-

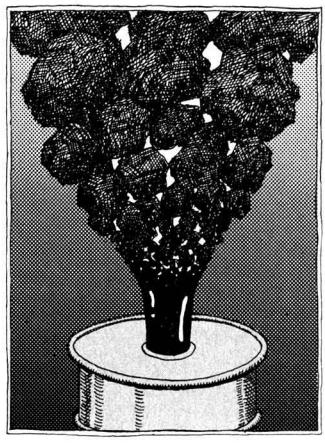
vironmental pollution. With great indulgence, they accepted my condition that all the examples of pollution should be from their own plants. As a practical illustration of "repentance," we filmed the treatment of sludge from one of their processes and followed through the extraction from it of rare metals and fine chemicals. Directors of I.C.I. who saw the film were piqued when they recognised that, for other purposes of the combine, they had been buying them at premium prices from competitors.

We are a long way past the time when we despised "erastz." The feudal hierarchy of traditional materials has now given way to an aristocracy of man-made alternatives. Or maybe one should say that materials have been democratised. I am old enough to remember when rayon was disparaged as "artificial silk," but no one would so derogate present man-made fibres. Polymer chemistry has produced a social revolution. It was summed up on a university debate, apropos of a famous British department store where Royalty and commoners shop for "ersatz." The motion was "This house agrees that Marks and Spencers have had more social influence than either Karl Marx or Herbert Spencer."

Synthetics

Apart from wood, structural materials were always inorganic. We even define our epochs as the Old Stone Age, the New Stone Age, the Bronze Age, and the Iron Age—the materials by which cultures were determined. Surely ours must be the Plastic Age, even if in terms of end results the products may be, in many cases, rigid and unyielding. We might agree that to qualify as a plastic or synthetic, the material, at some stage of its history, must possess plasticity, the capacity to flow and take a desired shape. The foundations of the present synthetic plastics industry were truly laid by Dr. Leo H. Baekerland when he produced the first man-made resin—phenoformaldehyde—in the presence of an acid catalyst.

Synthetic material, to match specific needs and process engineering requirements, challenged the metallurgists to make unmanageable metals manageable metals. Electrolysis had already transformed aluminum from an intractable laboratory curiosity,



tantalisingly described by Humphry Davy at the beginning of the last century, into a cheap universal light metal. Magnesium, lighter still, had been mass extracted from seawater. But, came the day when high temperatures, high speeds, and the new requirements of atomic energy and electronics called for the handling of unfamiliar metals such as uranium, beryllium, zirconium, titanium, germanium, indium, tantalum, niobium, and molybdenum. And—how important now—a new look at silicon.

Inside-out smelting, which uses ultra-short waves to agitate molecules and generate heat from inside a metal, made still rarer refinements possible. Powdered metallurgy, which involved compressing rather than smelting, produced combinations that could not be achieved by alloys. Ceramic metals, or metallic ceramics, a long way from potters' clay, exploited oxides, borides, carbides, and nitrides to make materials which were strong, corrosion resistant, and able to endure high temperatures. Combinations of plastic with metals or glass (e.g., fiberglass) opened up even wider possibilities.

The development of "tailor-made molecules" or, in the language of the new chemist, "long-chain polymers," was, indubitably, one of the most important points of departure in the history of technology. To be able to prescribe a material for a specific purpose and give it predetermined qualities meant that invention was taking on a new dimension. It was no longer a case of "What can we do with the metals we have?", but "What exactly do you want?"

Carbon fibre composites

One development that fascinates me is carbon fibre. (You see how compulsively I go back to coal and soot?) Since the advent of stressed skin construction in the early 1930's, aluminum alloys have been the dominant structural materials. They have been improved progressively. What designers of airframes are looking for is a structural material that combines strength, stiffness, weight, ease of fabrication, and durability under service conditions.

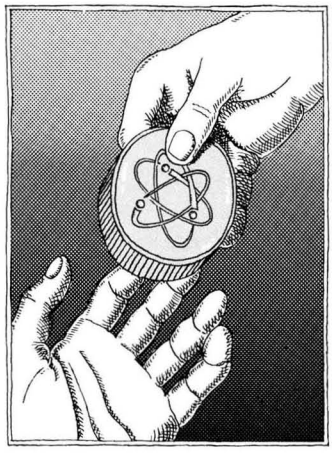
In all those requirements, carbon-fibre composite is five times more strong and four times more stiff than titanium alloy. Carbon-fibre epoxy is laminated so that the fibres are cross-plied. Substantial weight savings should result from the use of carbon-fibre composites as structural materials. Since the 1960's when they were first developed, activity has built up in the western world on their production and use not only in aircraft production but in manifold different ways, from self-lubricating bearings to golf clubs.

Using such a material, it is possible to reduce the vast number of small components that are typical of conventional metallic structures, leading to a reduction in production costs as well as weight. Laboratory tests have shown that this material does not exhibit fatigue properties analogous to those of metallic materials, but careful tests are still being carried out on the effects of temperature, moisture, and repeated loading under service conditions. The promise is that there will eventually be a weight saving of 25% in the wing structure compared with present materials.

Age changing

There may be those who might question the description the "Plastic Age" and make claims for the "Silicon Age." Identified with silicon chips and the implications that the integrated circuits they minisculise may take over the logical faculties of the human brain in a world run by computers, silicon might indeed qualify. Silicon stands next to carbon in the fourth group of the periodic system, and it is the second most abundant element in the earth's crust, surpassed only by oxygen. It is nonmetallic in character. It is present in practically every rock.

If we think back to the creation of the world, the respective roles of carbon and silicon are interesting. The carbon series build up their complex-



ities by conjunction of carbon atom to carbon atom, while the silicon series build up their complexities through the intermediary of oxygen atoms. In the beginning, at temperatures of −50 to +100 °C, carbon had within itself the capacity of evolving life, while silicon was a parent of cold rocks. The energy we get through the carbon route, like oil and coal, has come to us through the organic chemists. Silicon, long the inert material that as SiO (silica) fashioned glass and ceramics, was electrified by the solid-state physicists. Not only is silicon likely to run our businesses for us, but, with silicon cells already proven as the source of energy for the radiotransmitters and telemetering equipment of space satellites and probes, we can get direct conversion of sunbeams into electricity.

We are discussing materials and energy. The prevailing paradigm is that it all began with the Big Bang. Time began with a primaeval atom that exploded and released the energy and particles, the matter and antimatter, which formed the expanding universe, and all the galaxies and the stars and the planets and created the elements which congealed to form the earth. Energy into matter. Matter into energy.

When you are thinking about materials it does not matter whether you start with the energy within the nucleus or with hydrogen with its proton and orbiting electron. To have the elements that form any of the materials you are going to manipulate or the molecules you are going to fabricate you have to account for energy. You can do your accountancy in gigajoules or you can express it as money and costs "added value." But you have to do the sums properly, and what we call "cost" is not a reliable indicator. It all depends on "energy in" and "energy out."

For example, the food calories of a crop may be much less than the energy put into the artificial fertilisers. Or another example, the EEC produced an energy plan that aimed at 200 GW from nuclear reactors by 1990 (to help fill the predicted energy gap). One of my noble colleagues—an eminent scientist—in a select committee of the House of Lords, without bothering about the huge cost in money terms, demolished the argument by demonstrating on a sheet of notepaper that the energy used in the materials for constructing and equipping the many installations would exceed Europe's interim capacity and precipitate the energy shortage which the programme was planned to correct.

Perhaps if we really started accounting in energy terms instead of money symbols we might get the energy problem straight and get the real value of our materials and commodities. I ought to admit, and my banker will confirm, that I know little about finance, but I know that money has little relation to real wealth. It did at one time when the tillers produced the food calories and sustained the artisans who made better tools or better pots or better textiles than they could. The tiller bartered food for the products into which the artisan put his muscle energy.

And presently both the tillers and the artisans produced surpluses, which went onto trade barter between individuals and with other communities. Individuals could justify their efforts to each other—so much stoop labour was worth so much bench labour. But it was clumsy—so coins were invented and there was buying and selling. When goods were exported to other communities, there were further difficulties.

So Darius II of Persia invented the cheque (of Persian origin) or money order which said, "This barley is worth so much in Babylon and should be worth so many hides in Ispahan." The money became itself a commodity. Bankers started in Babylon as early as 500 B.C. They grub-staked the artisans. They paid people to dig irrigation canals and sold the water to the farmers. They discounted the cheques of the merchants on the caravan routes. There was a trade in money itself. It was not a question of the energy put into the product but of how much the market would bear.

Now, baffled by the apparent meaninglessness of money in real terms, by the wild excesses of inflation, and by the contortions of the financiers and economists to control, I have decided to go back to first principles—to the Big Bang, to $E = mc^2$—and invent my own currency, not based on the inert metal gold, dug out of one hole and stored in another, but on energy.

I follow the conventions of currency. It has to be something difficult to obtain; it has to be durable; and, by my specification, it has to be redeemable as energy. And it has to be calibrated. I decided on uranium-235. (Natural uranium is too accessible and plutonium is a second-stage product. I wanted a primary.)

^{235}U can be expressed in curies as gold can be expressed in carats. It can be calibrated to other forms of energy—coal and oil calories or food calories. It can be related in work terms to gigajoules. It can scarcely be carried around in the pocket, but it can be banked like the gold in Fort Knox, as the backing of notes. And it fulfils my last requirement—it can, in the ultimate, be put in reactors to produce energy. I have called my new currency "The Utope." You can derive it as you wish from "Uranium Isotope" or from "Utopia."

And it has as much promise of success as sunbeams out of cucumbers.

Acknowledgment

The Lord Ritchie-Calder plenary address is reproduced from *The Proceedings of the International Materials Congress: Materials Aspects of World Energy Needs* (1979), with the permission of the National Academy of Sciences, Washington, D.C.

Lord Ritchie-Calder *is a British writer, university professor, Baron (Life Peer) of Balmashannar, and listed in International Who's Who.*

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ES&T RESEARCH

Effect of Suspended Sediments on the Photolysis of Organics in Water

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■ An assessment of the role of suspended sediments and clays on the rate and mechanism of photolysis of pollutants in water was carried out. It was found that even though semiconductor powders such as TiO_2 could photocatalyze the decomposition of organics such as methyl alcohol and *p*-dichlorobenzene in water, no such reaction occurred with naturally occurring suspended sediments or clays. The sediments and clays were found to decrease the rate of photolysis of pollutants such as methoxychlor by shielding the pollutant from the available light.

Photolysis is an important route of environmental degradation for many organic pollutants such as pesticides (*1*). To date, most research has been focused on measuring photolysis degradation rates in mixed solvents and distilled water (*2*). However, in the environment varying amounts of suspended sediments are present in the water and this sediment could change the rate or mechanism of photolysis of a pollutant in several ways. Suspended sediment may reduce the photolysis rate by either shielding the organic from the available light or by quenching the excited states of the organic molecules before they react to form products. It is also possible for suspended particulates to enhance the rate of organic photolysis if sediment absorption of light produces excited states or free radicals that can then react with the organic. In this way it is possible for organic materials that do not absorb sunlight to be photolyzed indirectly.

This type of indirect photolysis does occur with semiconductors such as TiO_2, which are common constituents of clays, sediments, and soils (*3*). In the presence of O_2, ultraviolet (UV) irradiation of TiO_2 photooxidized alkanes to alcohols, aldehydes, and ketones (*4*). Also, UV irradiation of aqueous TiO_2 slurries results in the dehalogenation of fluorinated benzenes (*5*) and polychlorinated biphenyls (*6*). Similar reactions have also been observed for some semiconductors such as ZnO (*7*). It has been reported that the speed of photolysis of certain pollutants is much higher in natural waters than in distilled water owing to the presence of unknown sensitizers (*8, 9*). This paper reports studies designed to elucidate whether suspended sediments accelerate the photolysis of aqueous organics by a mechanism analogous to photosensitized semiconductor reactions or whether they slow down photoreactions by shielding or quenching.

Experimental

Some commonly found clays (montmorillonite, kaolinite, bentonite, dolomite, and illite) were obtained from Ward Scientific, and several samples of suspended sediments from rivers flowing into the Great Lakes were collected and freeze-dried. For comparison purposes, a sample of TiO_2 (anatase) powder was obtained from Fisher Scientific. The ultraviolet–visible adsorption spectra of the clays, sediments, and semiconductors were measured using a Pye-Unicam SP 1700 spectrophotometer equipped with a diffuse reflectance attachment. All spectra were referenced to magnesium oxide.

Aqueous solutions were irradiated as 1.0% slurries in a stirred quartz reaction vessel in a Rayonette photoreactor equipped with 300- or 350-nm ultraviolet lamps. The intensity of light impinging on the cell was 4.3×10^{-5} Einsteins/min at 300 nm and 6.3×10^{-5} Einsteins/min at 350 nm as measured by ferrioxalate actinometry (*10*).

The Fe(II) yields were determined from the absorbance at 510 nm ($A = 1.09 \times 10^4$) using *o*-phenanthroline and a neutralization–dilution technique (*11*). Formaldehyde concentrations were measured colorimetrically ($A = 1.8 \times 10^4$ at 470 nm) using a modified chromotropic acid technique (*12*) after suspended sediments were removed by centrifugation. After extraction of the 100 mL of slurry into 20 mL of pentane, the dichlorobenzene concentrations were measured using a Tracor 550 gas chromatograph equipped with an electron capture detector. A glass column packed with 10% OV-1 on Gas-Chrom Q was used isothermally at 130 °C for the analysis. Methoxychlor was determined using the same extraction and gas chromatographic procedure, except the temperature of the column was programmed from 230 to 330 °C at a rate of 5 °C/min with a final hold of 4 min.

Results and Discussion

The absorption spectra of a typical suspended sediment, clay, and semiconductor are shown in Figure 1. All the materials absorbed light strongly in the ultraviolet spectral region, but the semiconductor (TiO_2, anatase) showed a sharp cutoff in absorption at about 400 nm, corresponding to the band gap energy, whereas the suspended sediment and clay continued to absorb a significant amount of light in the visible region of the spectrum. These spectra were typical of various materials studied, although the wavelength dependence of the extinction coefficients varied significantly for the different suspended sediments and clays. To examine whether light absorption by these solids could lead to photoreactions, experiments were carried out with various scavengers that react with the photochemically produced free radicals to give readily identifiable products.

The first scavenger system employed was a degassed aqueous solution of isopropyl alcohol (0.26 M), methyl alcohol (0.49 M), ferric perchlorate (0.01 M), and perchloric acid (0.5 M). This system was chosen because the solution absorbs minimally at the irradiation wavelength (350 nm) and because alcohols are excellent scavengers for most oxygen-containing free radicals (*13, 14*). From studies of iron photochemistry (*11*) alcohol concentrations were selected that were large enough

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Table I. Iron(II) Quantum Yields of 1% Slurries of Clays and TiO_2 in the Aqueous Solution[a]

material	Fe(II) yield	material	Fe(II) yield
blank	0.032	kaolinite	0.0022
TiO_2 (anatase)	0.200	montmorillonite	0.0048

[a] $[HClO_4]$ = 0.5 M, $[CH_3OH]$ = 0.49 M, $[(CH_3)_2CHOH]$ = 0.26 M, $[Fe^{3+}]$ = 0.01 M. Irradiation wavelength, 350 nm.

Table II. Formaldehyde Quantum Yields for 1% Slurries of Suspended Sediments and TiO_2 in the Aqueous Solution 10% Methanol (Irradiation Wavelength, 300 nm)

material	formaldehyde quantum yield	
	degassed	air saturated
blank	0.000 38	0.000 58
TiO_2 (anatase)	0.003 4	0.082 1
Black River S.S.	0.000 28	0.000 41
40-Mile Creek S.S.	0.000 15	0.000 23

to scavenge all free radicals in the solution. Typical reactions of hydroxyl radicals in this solution are:

$$\begin{matrix}(CH_3)_2CHOH \\ \text{or} \\ CH_3OH\end{matrix} + OH\cdot \rightarrow \begin{matrix}(CH_3)_2\dot{C}OH \\ \text{or} \\ \cdot CH_2OH\end{matrix} + H_2O \quad (1)$$

$$\begin{matrix}(CH_3)_2\dot{C}OH \\ \text{or} \\ \cdot CH_2OH\end{matrix} + Fe^{3+} \rightarrow \begin{matrix}(CH_3)_2C{=}O \\ \text{or} \\ H_2C{=}O\end{matrix} + Fe^{2+} + H^+ \quad (2)$$

It can be seen that the production of one hydroxyl radical in the system eventually leads to the production of one Fe^{2+} molecule. Thus, the addition of ferric perchlorate at concentrations large enough to react with all the alcohol radicals formed suppresses chain reactions and provides a simple analytical system (Fe^{2+} analysis). Perchloric acid must be added to prevent dimerization and polymerization of the hexaaquo iron(III) to species that absorb light at the irradiation wavelength (*11*) and to prevent adsorption of Fe^{3+} and Fe^{2+} onto the sediments. Unfortunately, this strongly acidic solution caused decomposition of some of the materials under study (all suspended sediments, some clays), but some useful information was obtained.

Table I shows the Fe(II) quantum yields for the stable materials. There is a small but measurable Fe^{2+} yield in the scavenger solution in the absence of solids due to a small amount of light absorption of the hexaaquo iron(III) charge-transfer band that produces hydroxyl radicals (*11*). The semiconductor, TiO_2, gave Fe^{2+} quantum yields well above the blank, whereas the montmorillonite and kaolinite clays gave Fe^{2+} yields below the blank. This indicates that the semiconductor is producing free radicals that are being scavenged in the system and that the clays do not produce such free radicals.

The next scavenger system tested was an aqueous solution of 10% methanol. Methanol should react with oxygen-containing free radicals to produce formaldehyde, for which a very sensitive analytical technique is available (*12*). Formaldehyde quantum yields at 300 nm are reported for a few materials in Table II. Again there is a small but measurable yield with the scavenger solution in the absence of solids due to the photolysis of methanol. The addition of suspended sediments to the solution resulted in a reduction in the formaldehyde yield. The addition of the semiconductor TiO_2 led to large increases in the formaldehyde yield. When oxygen, an excellent electron scavenger, is added to the system (air saturated) the formaldehyde yields in all cases are increased substantially over the degassed solutions. Again, the semiconductor, TiO_2, appears to be the only photoactive material with this scavenger system.

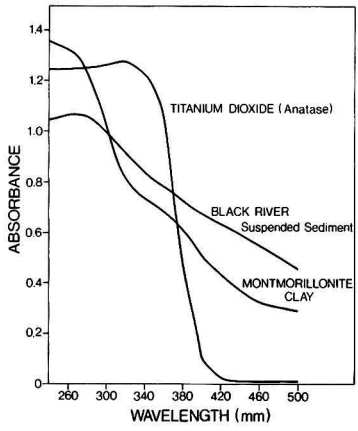

Figure 1. Ultraviolet–visible absorption spectra of TiO_2 (anatase), Black River suspended sediment, and montmorillonite clay

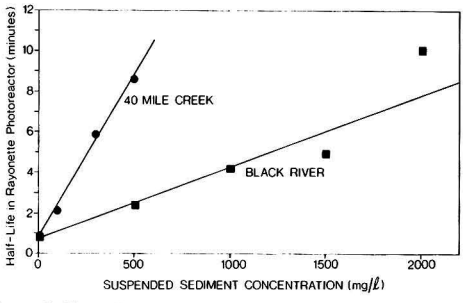

Figure 2. The effect of suspended sediment on the half-life of methoxychlor in a Rayonette photoreactor (wavelength of irradiation, 300 nm)

Since many of the persistent pollutants in natural waters are chlorinated compounds, an experiment was performed to see whether a chlorinated compound that did not absorb sunlight could be photodegraded when suspended sediment or clays were present. *p*-Dichlorobenzene (*p*-DCB) was chosen for study since it has an absorption maximum of 275 nm and does not absorb significantly at the wavelength of irradiation (300 nm). A saturated aqueous solution of *p*-DCB (47 ppm) was irradiated at 300 nm in the Rayonette photoreactor with 1.0% TiO_2 (anatase), and the *p*-DCB degraded rapidly with a half-life of approximately 5 min. When saturated aqueous solutions of *p*-DCB were irradiated as 1.0% slurries with the clays, montmorillonite, kaolinite, bentonite, illite, and dolomite, and with the suspended sediments from the Ausable, Grand, Black, and 40-Mile Rivers, no decomposition of the *p*-DCB was observed even after irradiation periods up to 4 h in the photoreactor. The irradiation of slurries of the naturally occurring titanium-containing ores, rutile and ilmenite, again resulted in no decomposition of the *p*-DCB from saturated aqueous solutions. Therefore, even though ultraviolet irradiation of the semiconductor, TiO_2, can result in the photodecomposition of non-light-absorbing organics in water, naturally occurring suspended sediments and clays do not appear to be capable of undergoing this type of photocatalytic reaction.

To find out what effect suspended sediments have on the photolysis rate of a compound that absorbs sunlight, the degradation rate of methoxychlor in the Rayonette photoreactor at 300 nm was studied as a function of suspended sediment concentration. Figure 2 shows that the rate of photodecomposition of methoxychlor from a saturated aqueous solution (0.12 ppm) is considerably reduced in the presence of the suspended sediments. The half-life of methoxychlor in the photoreactor seems to increase linearly with suspended sediment concentration but at different rates for the two sediments studied. Although there is a large difference in organic carbon content between the two sediments (40-Mile Creek, 21%; Black River, 4.1%), the major reason for the difference in behavior appears to be differential light absorption. The extinction coefficients at 300 nm, as measured in the secondary cell compartment of the spectrophotometer close to the photomultiplier, are 13.8×10^{-4} L mg^{-1} cm^{-1} for 40-Mile Creek and 4.1×10^{-4} L mg^{-1} cm^{-1} for Black River sediment. The true extinction coefficients of such suspensions are impossible to measure using a standard spectrophotometer because of sample light scattering. For example, if the measurement is made using the primary sample compartment of this spectrophotometer located some 15 cm from the photomultiplier, the apparent extinction coefficients are about twice the above values. In any case, the ratio of the extinction coefficients at 300 nm (30-Mile Creek/Black River) is about 3.3. The ratio of the slopes of the half-life vs. concentration plots (40-Mile Creek/Black River) is 3.8. Therefore, to a reasonably close approximation, the suspended sediments appear to be simply shielding the methoxychlor from the available light.

In summary, even though suspended sediments and clays can contain TiO_2 and other semiconductors in the 5–10% range and even though they absorb sunlight, suspended sediments and clays do not appear to photocatalyze the decomposition of organic pollutants in water but reduce the rate of photolysis by shielding the pollutant from the available light.

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Factor Analysis and Derivation of an Experimental Equation on Polynuclear Aromatic Hydrocarbon Emissions from Automobiles

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■ Factor analysis on polynuclear aromatic hydrocarbon (PAH) emissions from gasoline engine automobiles was made on the data from test runs of more than 50 000 km on each of 26 cars. The average emission rate of PAH from cars was directly linked to average car mileage. The consumption of engine oil was a significant factor governing PAH emissions from cars in ordinary city service. An experimental equation which can give the average emission rate of PAH from cars was derived as a function of car mileage and engine oil mileage. The validity of this equation was supported by field data.

Recently, carcinogenic polynuclear aromatic hydrocarbons (PAHs) from automobiles have become a significant problem for public health, especially in big cities troubled by heavy traffic. The present research is part of ongoing research on the emissions of PAHs from automobiles.

Generally, older cars with higher mileage have higher PAH emissions (*1–4*). For example, Begeman and Colucci (*1*) measured the emission rates of PAH from 25 cars. They showed that the average emission rate of benzo[*a*]pyrene (BaP) from 12 cars of 1951–1959 model years was 3 times higher than that from 13 cars of 1959–1963. Thus, PAH emissions are closely related to car age, i.e., car mileage.

To determine a quantitative relation between PAH emission rate and car mileage, test runs of more than 50 000 km were carried out on each of 26 Japanese gasoline engine cars in ordinary city service (*5*). In this paper, from the results of the test runs, we elucidated the main factors governing PAH emissions, and derived an experimental equation on PAH emissions as a function of car mileage and engine oil mileage. Finally, the validity of this equation was evaluated by field data.

Experimental

To investigate the effect of used oil on PAH emission, two cars, car A and car B, were operated for 6000 km on single oil changes. For car A, a similar test run was repeated.

The specifications of these cars are as follows. Car A: 1972 model year, 4-cycle and 4-cylinder gasoline engine, 1400-cm^3 displacement, spark retarded for emission control of HC and NO_x, initial car mileage in the test run, 39 000 km, and consumption rate of engine oil, operating at 40 km/h using new oil, 1.44 mL/L of fuel (oil economy, 10.9 km/mL). Car B: 1974, 4-cycle and 4-cylinder gasoline engine, 1200 cm^3, spark retarded, 19 000 km, and 0.14 mL/L of fuel (143 km/mL) at 40 km/h using new oil.

The PAH measurements were made at 2000-km intervals

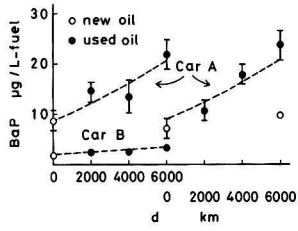

Figure 1. BaP emission rate under 40 km/h operating condition vs. oil mileage (d). Broken lines: calculated results

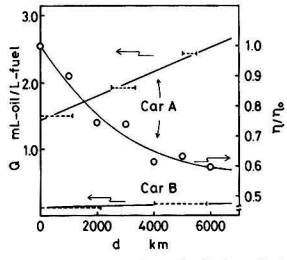

Figure 2. Oil consumption rate (Q) and relative oil viscosity vs. oil mileage. Broken lines: kilometers where oil consumptions were measured

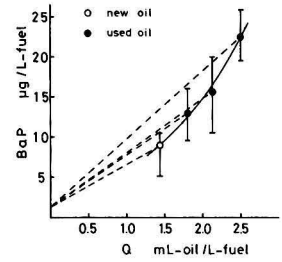

Figure 3. BaP emission rate vs. oil consumption rate for car A

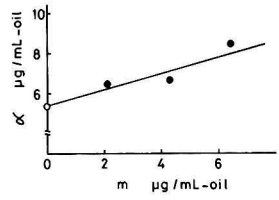

Figure 4. Rate of generation of BaP from consumed oil vs. concentration of BaP in oil for car A

during the above test runs. The sample collection was done on a chassis dynamometer, while operating at 40 km/h.

The fuel used in the test runs and the PAH measurements was the same commercial gasoline containing 153 μg/L BaP and no tetraethyllead. The lubricating oil used for the tests was the same commercial oil, which had only negligible traces of PAH in its fresh condition.

With respect to the test runs of 26 cars and the measurements of PAH from them for the investigation on the relationship between PAH emission and car mileage, the details have been described in a previous paper (*5*).

The procedures for the PAH collection from automotive exhaust gas and the PAH analysis have also been described there (*5*).

Results and Discussion

Relationship between PAH Emission and Oil Mileage. It has been shown previously (*5*), from the results of the measurements for the 26 cars, that PAH emissions under used oil conditions were, on the average, higher than those under new oil conditions. Furthermore, we investigated the relationship between BaP emission and engine oil mileage, and the causes of the higher emission under used oil conditions, using two cars, i.e., car A with a comparatively high oil consumption rate and car B with a low consumption rate.

As Figure 1 shows, the BaP emission rate for car A increased with an increase in the oil mileage. The higher emission level after the 6000-km run returned to the initial low level after changing the oil. When the 6000-km test was repeated for car A, a similar result was obtained. On the other hand, this increase was hardly noticed through the test run of 6000 km for car B.

The above increases for car A are considered to be due to an increase in oil consumption rate by aging of oil, because it is known that high oil consumption causes high PAH emission (*1*, *5–8*). As Figure 2 shows, for car A, a considerable increase in oil consumption rate was observed in proportion to the oil mileage. For car B, a slight increase was observed.

In order to find out the cause of the increase in the oil consumption rate for car A, a change of the viscosity of the oil with oil mileage was investigated. The relative viscosity of the oil, η/η_0, decreased with an increase in oil mileage, where η and η_0 are the viscosities of used oil and new oil, respectively. This result is also shown in Figure 2. Therefore, the increase in oil consumption rate with the increase in oil mileage is due to the lowering of oil viscosity.

The reciprocal of the above relative viscosity was found to increase linearly with the increase in oil mileage. That is, η_0/η can be given by:

$$\eta_0/\eta = \gamma d + 1 \qquad (1)$$

where γ is a proportionality constant and d represents kilometers of oil use. γ was given as 1.25×10^{-4} km^{-1} for car A.

It is known that oil consumption rate is inversely proportional to oil viscosity (*9*), i.e., $Q = Q_0\eta_0/\eta$, where Q and Q_0 are oil consumption rates for used oil and new oil, respectively. From this relation and Equation 1, the following equation is given:

$$Q = Q_0(\gamma d + 1) \qquad (2)$$

Q and Q_0 are expressed in units of mL of oil consumed/L of fuel consumed.

Provided that the elevation in the BaP emission level with the increase in oil mileage for car A depends only on the increase in the oil consumption rate, the plot of the BaP emission rate vs. the oil consumption rate should give a linear relation. However, the relation is not linear, as shown in Figure 3. The deviation from linearity is considered to be caused by the accumulation of BaP in used oil.

To estimate the emission rate of BaP only from consumed oil, the contribution (β) from factors other than engine oil was subtracted from each BaP emission rate in Figure 3. The β value was taken as 1.27 μg/L of fuel (Table I). The explanation of the determination of this value will be done in the succeeding section. Each estimated value was divided by the corresponding oil consumption rate. The result gives the rate of generation, α μg/mL, of BaP from 1 mL of consumed oil. The increase in the slope of the broken line in Figure 3 means the increase in α. (The common intercept for the broken lines was taken for the subtraction of β.) Each slope, i.e., α, was plotted vs. the concentration, m μg/mL, of BaP in the oil. As Figure 4 shows, the plot gave a straight line, with a slope of 0.375 (nondimension) and an intercept of 5.40 μg/mL of oil.

The intercept gives the rate of generation of BaP from oil in its fresh condition, which equals the intrinsic rate of formation, α_0 μg/mL, of BaP from consumed oil for car A, because the content of BaP in the new oil was negligible. The slope represents the ratio, p, of BaP surviving the emission process in consumed oil. That is, for car A, about 38% of the BaP contained in the oil consumed by leakage into the combustion chamber or the exhaust system survived the emission process. From the linearity in Figure 4, the rate of generation, α, of BaP from used oil can be written as follows:

$$\alpha = pm + \alpha_0 \quad (3)$$

In order to confirm further the effect of the PAH in oil on the PAH level in exhaust gas, another experiment was done by adding BaP artificially to new oil. As Figure 5 shows, for car A, BaP emission rate increased linearly with an increase in the concentration of BaP in the oil. The survival ratio, p, of BaP in the consumed oil was given by dividing the slope, 0.480 mL of oil/L of fuel, of the straight line by the oil consumption rate, 1.44 mL/L of fuel, for the new oil condition. The result was 0.333. This value agreed approximately with the value obtained from the plot in Figure 4. The mean of them, 0.354, was adopted as p for car A.

On the other hand, for car B with a low oil consumption rate, the effect of BaP in oil was scarcely recognized, as shown in Figure 5.

The actual mode of accumulation of BaP in engine oil was followed by the quantitative analysis of BaP in the oil at every 1000 km during the run of 6000 km. The concentration of BaP accumulated in oil was found to be directly proportional to oil mileage, d km. A similar result was shown by Gross (7), too. Hence, the concentration, m μg/mL, of BaP in engine oil was given by:

$$m = \delta d \quad (4)$$

where δ is the accumulation rate of BaP in oil. Its values were given as 1.10×10^{-3} and 1.21×10^{-3} μg/(mL·km) for car A and car B, respectively.

On the basis of the results described so far, an experimental equation, which can explain the change of BaP emission rate with oil mileage, was derived:

$$\mu g \text{ of BaP/L of fuel} = \alpha Q + \beta = Q_0(\gamma d + 1)(\alpha_0 + pm) + \beta = Q_0(\gamma d + 1)(\alpha_0 + p\delta d) + \beta \quad (5)$$

Upon substituting the numerical values for the individual coefficients in this equation, the equation was written as a quadratic function of d. The equations for an operating condition of a steady speed of 40 km/h on car A and for that on car B are as follows: on car A,

$$\mu g \text{ of BaP/L of fuel} = 7.01 \times 10^{-8} d^2 + 1.53 \times 10^{-3} d + 9.05 \quad (6)$$

($Q_0 = 1.44$ mL of oil/L of fuel, $\gamma = 1.25 \times 10^{-4}$ km^{-1}, $\alpha_0 = 5.40$ μg/mL of oil, $p = 0.354$, $\delta = 1.10 \times 10^{-3}$ μg/(mL·km), $\beta = 1.27$ μg/L of fuel), and on car B,

$$\mu g \text{ of BaP/L of fuel} = 8.05 \times 10^{-9} d^2 + 1.88 \times 10^{-4} d + 2.17 \quad (7)$$

($Q_0 = 0.14$ mL/L, $\gamma = 1.50 \times 10^{-4}$ km^{-1}, $\alpha_0 = 6.40$ μg/mL, $p = 0.317$, $\delta = 1.21 \times 10^{-3}$ μg/(mL·km), $\beta = 1.27$ μg/L). For the values of β on car A and γ, α_0, p, and β on car B, the average values (Tables I and II) determined using the 26 cars were used.

As shown in Figure 1, the results calculated from Equations 6 and 7 were in good agreement with the observed values for car A and car B, respectively.

For cars with low oil consumption such as car B, since the contribution from the first and second terms in Equation 7 is small as compared with the value of the final term, the effect of used oil is not so apparent. However, for cars with high oil consumption, its effect becomes significant.

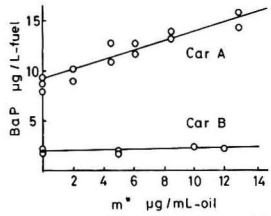

Figure 5. BaP emission rate vs. concentration (m^*) of BaP added in new oil

Table I. Values of $\bar{\alpha}_0$ and $\bar{\alpha}$ (μg/mL of Oil) and $\bar{\beta}_0$ and $\bar{\beta}$ (μg/L of Fuel), for 10-Mode and 40 km/h Conditions

		$\bar{\alpha}_0$	$\bar{\alpha}$	$\bar{\beta}_0$	$\bar{\beta}$
BaP	10-mode	5.47	6.19	1.62	1.85
	40 km/h	6.40	7.03	1.25	1.27
BaA	10-mode	13.4	15.3	14.2	15.6
	40 km/h	15.0	17.2	13.6	14.9
chrysene	10-mode	13.9	15.9	17.0	17.2
	40 km/h	16.0	17.9	14.6	16.4
pyrene	10-mode	33.4	63.4	97.4	99.2
	40 km/h	41.7	70.9	95.7	107

Average PAH Emission Rate as a Function of Average Car Mileage. The change of PAH emission rate (BaP, benz[a]anthracene (BaA), chrysene, and pyrene) with car mileage was studied by test runs of more than 50 000 km on each of 26 cars. The details of the results have been reported previously (5). A quantitative analysis of the results is made here. Emission rates of PAH from cars, even from the cars with almost similar mileage, varied over a wide range (5). The mode of the change of PAH emission rate with car mileage also differed widely among individual cars (5). However, taking an average in the groups of cars, a linear relation between the average PAH emission rate and the average car mileage was recognized at mileages above 20 000 km, with a correlation coefficient of more than 0.95 (statistically significant at a confidence level of more than 95%).

A linear relation between average PAH emission rate and average oil consumption rate was also recognized for each condition of new and used oil, with a correlation coefficient of more than 0.96 (statistically significant at a confidence level of more than 95%). That is, this relation can be expressed by the following equations:

$$\mu g \text{ of } \overline{j\text{-PAH}}\text{/L of fuel} = \overline{\alpha}_{0j}\overline{Q}_0 + \overline{\beta}_{0j} \text{ (new oil)} \quad (8)$$

and

$$\mu g \text{ of } \overline{j\text{-PAH}}\text{/L of fuel} = \overline{\alpha}_j\overline{Q} + \overline{\beta}_j \text{ (used oil)} \quad (9)$$

The subscript j means a PAH species. $\overline{Q}_0$ and $\overline{Q}$ (mL/L of fuel) are average oil consumption rates for new oil and used oil conditions, respectively. The slopes, $\overline{\alpha}_{0j}$ and $\overline{\alpha}_j$ (μg/mL of oil), give the average intrinsic rate of formation and the average rate of generation of j-PAH from consumed oil for its new and used conditions, respectively. The intercepts, $\overline{\beta}_{0j}$ and $\overline{\beta}_j$ (μg/L of fuel), indicate the contribution of j-PAH from factors other than consumed oil, presumably mainly from gasoline, under new oil and used oil conditions, respectively. The numerical values of $\bar{\alpha}_0$, $\bar{\alpha}$, $\bar{\beta}_0$, and $\bar{\beta}$, which were determined by a least-squares method, are summarized in Table I.

The values of $\bar{\beta}$ were slightly higher than those of $\bar{\beta}_0$. How-

Table II. Values of $\bar{m}$ (μg/mL of Oil), $\bar{p}$, and $\bar{\delta}$ (μg/(mL·km))

	$\bar{m}$	$\bar{p}$ 10-mode	$\bar{p}$ 40 km/h	$\bar{\delta}$
BaP	1.99	0.362	0.317	7.65×10^{-4}
BaA	6.12	0.310	0.359	2.35×10^{-3}
chrysene	6.63	0.302	0.287	2.55×10^{-3}
pyrene	107	0.280	0.273	4.12×10^{-2}

Table III. Values of $\bar{\lambda}_0$ and $\bar{\lambda}$ (mL/(L·km)) and $\bar{D}_0$ (km)

	$\bar{\lambda}_0$	$\bar{\lambda}$	$\bar{D}_0$ new oil	$\bar{D}_0$ used oil
10-mode	6.47×10^{-5}	8.96×10^{-5}	19 210	20 830
40 km/h	1.03×10^{-4}	1.44×10^{-4}	19 960	20 460

ever, the difference between them was of no great importance.

The values of $\bar{\alpha}$ were higher than those of $\bar{\alpha}_0$. This can be ascribed to the contribution of the PAH accumulated in used oil. The average mileage of the used oils employed for the present PAH emission tests was 2600 km. The average concentrations, $\bar{m}$ (μg/mL), of PAH in the used oils are summarized in Table II. The concentration of pyrene in used oil was much higher than those of the others. This caused the remarkable difference between $\bar{\alpha}$ and $\bar{\alpha}_0$, particularly for pyrene.

The average survival ratio, $\bar{p}_j$, of j-PAH in consumed oil was determined from $\bar{\alpha}_{0j}$, $\bar{\alpha}_j$, and $\bar{m}_j$ by Equation 3.

The average accumulation rate of j-PAH in engine oil, $\bar{\delta}_j$, μg/(mL·km), was determined from $\bar{m}_j$ and the average mileage $\bar{d}$ (2600 km) by Equation 4. The values of $\bar{p}$ and $\bar{\delta}$ are summarized in Table II.

The relationship between the average oil consumption rate and the average car mileage, $\bar{D}$ km, could be adequately approximated at mileages above 20 000 km by the following linear equation, with a correlation coefficient of 0.97 (statistically significant at a confidence level of 95%), for each condition of new and used oil:

$$\bar{Q}_0, \text{ mL/L of fuel} = \bar{\lambda}_0(\bar{D} - \bar{D}_0) \text{ (new oil)} \quad (10)$$

and

$$\bar{Q}, \text{ mL/L of fuel} = \bar{\lambda}(\bar{D} - \bar{D}_0) \text{ (used oil)} \quad (11)$$

The numerical values of the coefficients $\bar{\lambda}_0$ and $\bar{\lambda}$ (mL/(L·km)) and $\bar{D}_0$ (km), which were determined by a least-squares method, are summarized in Table III. The values of $\bar{D}_0$ were in fairly good agreement regardless of new/used oil, 10-mode (the standard Japanese city driving schedule)–40 km/h operation. The average was 20 120 km. From Equations 2 and 10:

$$\bar{Q} = \bar{Q}_0(\bar{\gamma}\bar{d} + 1) = \bar{\lambda}_0(\bar{\gamma}\bar{d} + 1)(\bar{D} - \bar{D}_0) \quad (12)$$

Upon comparing Equations 11 and 12:

$$\bar{\lambda} = \bar{\lambda}_0(\bar{\gamma}\bar{d} + 1) \quad (13)$$

The value of $\bar{\gamma}$ was determined from those of $\bar{\lambda}_0$ and $\bar{\lambda}$, and $\bar{d}$ = 2600 km by Equation 13. The determined values for 10-mode and 40 km/h conditions were 1.48×10^{-4} and 1.52×10^{-4} km^{-1}, respectively. These values can be regarded to be in fairly good agreement. Therefore, their average, 1.50×10^{-4} km^{-1}, was adopted as the value of $\bar{\gamma}$.

From the results obtained so far, an experimental equation

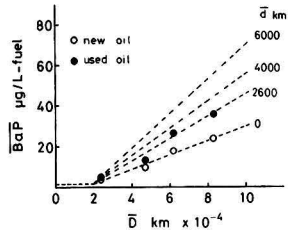

Figure 6. Average BaP emission rates calculated for various average oil mileages and observed ones vs. average car mileage. Broken lines: calculated results

on the average emission rate of PAH from gasoline engine cars was derived as a function of average car mileage $\bar{D}$ and average oil mileage $\bar{d}$ by the modification of Equation 5. The derived equation is as follows:

$$\overline{j\text{-PAH emission rate}} \text{ (μg/L of fuel)} = \bar{\alpha}_j\bar{Q} + \bar{\beta}_j$$
$$= \bar{\lambda}_0(\bar{\gamma}\bar{d} + 1)(\bar{D} - \bar{D}_0)(\overline{\alpha_{0j}} + \bar{p}_j\bar{\delta}_j\bar{d}) + \bar{\beta}_j \quad (14)$$

Upon substituting the numerical values for the individual coefficients in this equation, the equation was transformed into the feasible form of a linear function of $\bar{D}$ and a quadratic function of $\bar{d}$. For example, the equation for average emission rate of BaP from cars operated on the 10-mode city driving cycle is as follows:

$$\mu\text{g of } \overline{BaP}\text{/L of fuel} = (2.69 \times 10^{-12}\bar{d}^2 + 7.10 \times 10^{-8}\bar{d}$$
$$+ 3.54 \times 10^{-4}) \times (\bar{D} - 20\,120) + 1.85$$
$$\bar{D} \geq 20\,120 \quad (15)$$

($\bar{\lambda}_0 = 6.47 \times 10^{-5}$ mL/(L·km), $\bar{\gamma} = 1.50 \times 10^{-4}$ km^{-1}, $\overline{\alpha_0} = 5.47$ μg/mL of oil, $\bar{p} = 0.362$, $\bar{\delta} = 7.65 \times 10^{-4}$ μg/(mL·km), $\bar{\beta} = 1.85$ μg/L of fuel, $\bar{D}_0 = 20\,120$ km).

Figure 6 shows the results calculated by Equation 15 for various $\bar{d}$ and $\bar{D}$ values. The experimental values of the average BaP emission rate under 10-mode operating conditions were also plotted vs. $\bar{D}$ in Figure 6. There was good agreement between them, for both conditions of new oil ($\bar{d}$ = 0) and used oil ($\bar{d}$ = 2600 km).

For cars with low car mileages below 20 000 km, PAH emission rates were very low. The emission rates of BaP from them were a few micrograms per liter of fuel.

Evaluation of the Equation by Field Data. The validity of Equation 14 was evaluated by comparing the calculated results with those observed in the actual atmospheric environments, where pollution by PAH from gasoline engine cars was considered to be predominant.

The PAH concentrations in the actual environments were measured at Iidabashi along Sotobori St. in Tokyo in December 1977 and Chiyoda Road Tunnel on the Metropolitan Expressway in August 1977. The PAH collection at Iidabashi was done with an apparatus additionally equipped with liquid nitrogen cooling traps after the filter to capture PAH which passed through the filter. The collection in Chiyoda Tunnel was done with an ordinary high-volume air sampler. The results are summarized in Table IV.

The average emission rates of PAH from cars in ordinary city operation were estimated on the basis of Equation 14 in the following manner. The average mileage of cars in Tokyo, $\bar{D}$, was estimated to be 43 600 km from the number of gasoline engine cars registered each year (*10*) and the average mileage accumulation per year, 13 000 km. The value of 13 000 km was estimated from the average kilometers driven by gasoline engine cars per day in Tokyo, 36.7 km, based on the traffic statistics of the Metropolitan Police Office (*11*).

The average oil mileage, $\bar{d}$, was estimated to be 1950 km as the middle value of the average oil change interval of 3900 km.

Table IV. Observed and Calculated Atmospheric PAH Concentrations

		obsd concn, ng/m³			
		BaP	BaA	chrysene	pyrene
Iidabashi	filter	2.68	6.14	7.05	13.7
	liq. N_2 traps	0.19	0.92	1.41	16.2
	total	2.87	7.06	8.46	29.9
Chiyoda Tunnel	filter	14.2	14.0	19.3	31.7
		calcd concn, ng/m³			
Iidabashi		2.12	6.24	6.58	28.4
Chiyoda Tunnel		10.9	32.0	33.8	146

Table V. Average Car PAH Levels Calculated by Equation 14

	BaP	BaA	chrysene	pyrene
μg/L of fuel	22.8	67.1	70.9	306
μg/m³	2.39	7.05	7.44	32.1

The value of 3900 km was estimated on the basis of the data of the Petroleum Association of Japan (*12*).

The driving modes of cars at Iidabashi on Sotobori St. and in Chiyoda Tunnel were close to a steady rate of 40 km/h. Therefore, the calculation of the average PAH emission rate from cars was done regarding the condition of 40 km/h. The results are summarized in Table V. In order to match the units of PAH emission rates with the ones of the PAH concentrations measured in atmospheric environments, the unit of μg/L of fuel was transformed into μg/m³ of exhaust gas. The results are also summarized in Table V.

Colucci and Begeman (*13*) and Hirono et al. (*14*) reported that, in high traffic areas, atmospheric BaP was significantly correlated with CO concentration. Therefore, it can be assumed that the dilution ratio of PAH from automotive exhaust to atmosphere is nearly equal to the dilution ratio of CO. The CO emissions from cars depended somewhat on car mileage. The average concentration of CO from cars under an operating condition of 40 km/h could be approximated by the following equation, with a correlation coefficient of 0.98 (statistically significant at a confidence level of 98%): $\% \overline{CO} = 2.0 \times 10^{-6}\overline{D} + 0.52$. Hence, the average CO concentration for $\overline{D}$ = 43 600 km was estimated to be 0.61%. The CO concentrations in Iidabashi and Chiyoda Tunnel were 5.4 and 27.7 ppm, respectively. Therefore, the dilution ratios in Iidabashi and Chiyoda Tunnel were given as 1/1130 and 1/220, respectively. The concentrations of PAH diffused from automotive exhausts into the atmosphere were calculated from the values in Table V and these dilution ratios. The results are summarized in Table IV.

The calculated concentrations of PAH for Iidabashi were in fair agreement with the observed ones. For Chiyoda Tunnel, the approximate agreement between the calculated and observed concentrations was recognized for BaP; however, agreement was not recognized for other lower molecular weight PAHs. As one cause of the disagreement, the incomplete collection of lower molecular weight PAH is considered. The sampling in Chiyoda Tunnel was carried out in summer. Therefore, the collection error may be larger than that in the sampling at Iidabashi in winter.

Thus, the validity of Equation 14 was supported by the field data. Consequently, the equation seems likely to be sufficient to give the average emission rate of PAH from gasoline engine cars in ordinary city operation.

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Chemical and Physical Behavior of Stabilized Scrubber Sludge and Fly Ash in Seawater

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■ An investigation of chemical and physical properties of a stabilized admixture of scrubber sludge and fly ash in seawater was carried out with the intent of relating the results to the question of ocean disposal of these wastes. Leaching studies indicated that stabilization minimized or prevented the release of copper, iron, and nickel. Release of major components, i.e., calcium salts, was regulated by solubility and surface: volume ratio of solid test samples. Studies of physical properties (porosity, density, compressive strength, surface hardness) carried out in the laboratory and the results of ongoing field work have demonstrated that the structural strength of test blocks is maintained over prolonged periods in seawater.

With the return of coal as a major energy source and the use of flue gas desulfurization scrubbers to remove sulfur oxides from the combustion gases generated, large quantities of scrubber sludge and fly ash will be produced by coal-fired electric utilities (*1*). These waste products have been found to be environmentally unacceptable for direct land or ocean disposal (*2*). However, they can be mixed with a suitable additive, such as lime, to form stabilized brick-like solids which may be useful materials in construction (*3, 4*). Another alternative would be to use blocks of stabilized scrubber sludge and fly ash (SSFA) to construct a subsurface ocean reef. This application would provide a habitat for marine life besides reducing the costs and problems associated with more conventional disposal. The purpose of the present investigation was to conduct a laboratory study of the chemical and physical behavior of SSFAs in seawater. The aim was to (a) measure concentrations of major and minor elements in test mixes, (b) determine physical properties, and (c) investigate leaching behavior of major and minor components.

A large scale, comprehensive field and laboratory research project resulting from this preliminary investigation is now underway at the Marine Science Research Center in which biological impacts and long-term block stability are being addressed.

Methodology

Test Mixes, Samples, and Composition. Test samples, which were solid cylinders 7.6 × 7.6 cm of SSFA, were prepared by IU Conversion Systems, Inc. (IUCS) of Philadelphia, Pa. The samples were cured at 23 °C and 80–90% relative humidity for at least 30 days prior to use. Four SSFA mix types were prepared to examine varying sample compositions. The basic mix design (Poz-O-Tec process by IUCS, Inc.) was as follows: 16% scrubber sludge + 80% fly ash + 4% quicklime. These mixes were especially designed for this project. For mix 6, 20% of the fly ash was substituted by bottom ash. The scrubber sludge used in mixes 4 and 5 was obtained from the Conesville power plant (Columbus and Southern Ohio Electric). The scrubber sludge for mixes 6 and 7 plus all of the fly ash and bottom ash used were obtained from the Elrama power plant (Duquesne Light) located near Pittsburgh, Pa. The ash:scrubber sludge ratio in these mixes was approximately 5:1. At present, work is continuing on 1:1 and 3:1 mixes that are more representative of the true waste ratios that would be generated at an operating flue gas scrubbing power plant.

Test samples of construction grade concrete prepared by ASTM methods (*6, 7*) and cured for 30 days were used for comparison purposes.

The cured samples of SSFA and concrete were ground using a porcelain mortar and pestle and analyzed for Ca, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn by atomic absorption spectrophotometry (AAS) (*7*). Sulfite (SO_3) was converted to sulfate (SO_4) and, subsequently, total SO_4 was determined gravimetrically by precipitation of $BaSO_4$. Total carbon was determined using a carbon–hydrogen–nitrogen analyzer and carbonate carbon was determined using a gas buret method (*8*).

Physical Properties. Permeability was determined using the standard falling head technique and the Darcy equation (*9*). Porosity and bulk specific gravity were determined from the change in weight of samples due to the absorption of water (*6*). Bulk densities of dried, powdered samples were determined by measuring the volume displacement of water per mass of material (*6*).

Compressive strength was determined by measuring the load needed to achieve total failure of the sample when the load was applied to the vertical axis of the sample (*6*). A Riehle universal testing apparatus with a loading rate of 0.064 cm/min was used.

Qualitative determination of the relative surface hardness of the test mixes was made using an improvised abrasion technique (*7*).

Sets of samples were tested for compressive strength and surface hardness after curing in humid air for: 30 days, 150 days, 120 days with 30 additional days of immersion in seawater, and 30 days with 120 days immersion in seawater; the salinity of the seawater was about 34‰.

Leaching Experiments. *Percolation Experiment.* To accelerate the dissolution process, a percolation leaching experiment (*10, 11*) was performed on mixes 5 and 7. The experiment consisted of percolating seawater through stabilized scrubber blocks while they were fixed in vertical pvc columns, 1 m in height (*7*). Seawater (2.5 L) was added to the columns, containing mixes 5 and 7, before the system was closed and purged with N_2 to avoid oxidation of SO_3 to SO_4. After percolation began, successive 60-mL aliquots of seawater were removed for analysis of pH, Eh, and the concentrations of Ca, SO_3, SO_4, Ni, Cu, and Fe (*7*).

Tank Experiment. In these experiments, samples of SSFA mixes 5 and 7 were placed in tanks with covers, containing 3 L of seawater, for 1 month without stirring to determine short-term leaching rates of major and minor soluble components from SSFAs. A control tank containing seawater alone was also sampled. Aliquots of seawater were withdrawn by plastic syringe at the beginning of the experiment and at the following time intervals: 1, 3, 5, 10, 20, and 30 days for analysis of pH, Eh, dissolved SO_3, SO_4, Ca, Cu, Fe, and Ni (*7*). The seawater was thoroughly mixed prior to sampling each time.

Results and Discussion

Composition. Concentrations of selected major and acid leachable minor components are presented in Table I. These values are average concentrations based on replicate samples and subsamples of each mix type. There was no significant variation [one-way ANOVA, $\alpha = 0.05$; Sokal and Rohlf (*12*)]

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Table I. Concentrations of Selected Major and Minor Components[a]

sample mix type	bulk content, mg/g				acid-leached components,[b] μg/g											
	$CaCO_3$	total carbon	CO_3 carbon	org carbon[c]	Ca	SO_3	SO_4[d]	Fe	Mn	Zn	Cu	Cr	Pb	Ni	Cd	Hg
4	118	15	14	1	52 200	23 600	2 600	3 660	58.6	23.2	19.1	16	11	7	0.6	0.048
5	118	17	14	3	66 600	26 700	3 000	4 750	53.0	30.5	22.7	18	19	7	0.7	0.059
6	15	20	2	18	33 200	16 300	24 500	4 930	35.1	13.7	12.3	7	12	6	0.4	0.272
7	19	25	2	23	37 400	16 300	24 500	3 340	33.1	14.1	10.9	10	10	3	0.2	0.299
concrete[e]					111 300		6 400	5 780	312.5	18.4	5.2	24	6	5	<0.2[g]	0.010
detection	5	1	0.5	1	400	100	100	30	0.3	0.1	0.4	2	3	2	0.2	0.002
C.V., %[f]	9.5	15.7	9.5	15.7	10.5	10.7	10.7	4.9	4.1	21.4	7.2	9.4	20.8	18.9	17.3	12.1

[a] Concentrations are presented on a dry weight basis and are average values of sample and subsample replicates. [b] Nitric acid was used for heavy metal leaching and hydrochloric acid was used for calcium and sulfur oxide leaching. [c] Organic carbon is determined by subtracting carbonate carbon from total carbon. [d] Total SO_x was measured analytically; reported values of SO_3 and SO_4 are based on SO_3:SO_4 ratios supplied by IUCS. [e] Concrete component concentrations are based upon total weight including aggregates. The component concentrations presented would be approximately two times higher if the aggregate materials were not included. [f] C.V. is the weighted average coefficient of variation ($SD/\bar{y} \times 100$) for the replicate samples ($n = 2$) and subsamples ($n = 3$) of each mix type for each component measured. [g] Less than sign denotes values below the detection limit.

Table II. Selected Physical Properties of Test Samples[a,b]

sample mix type	bulk density, g/cm³	bulk sp gravity	porosity, vol % of water-permeable voids	coeff of permeability K (cm/s) × 10^{-7}
4	2.17 (0.2)	1.48	34	3.9
5	2.18 (0.1)	1.49	37	1.0
6	1.99 (0.3)	1.01	58	
7	2.03 (0.2)	1.21	48	65.0
concrete	2.70 (0.05)	1.96	13	0.1

[a] All samples were cured 90 days. [b] Values in parentheses represent range between duplicate subsamples.

between samples of the same mix type for any of the components measured. Thus a fairly uniform product was achieved in the preparation of the test mixes.

Major Components. The four mix types investigated fell into two basic categories depending upon the power plant origin of the scrubber sludge used in each mix. Mixes 4 and 5 (Conesville scrubber sludge) had a higher $CaCO_3$ content, SO_3:SO_4 ratio, and a lower organic carbon residue than mixes 6 and 7 (Elrama scrubber sludge). These parameters are dependent upon the power plant characteristics, i.e., scrubbing process and boiler efficiency. The SO_3:SO_4 ratio of the mixes and the overall Ca content are two very important characteristics in the stability and behavior of SSFAs in seawater.

Minor Components. High SO_4 mixes were lower in heavy metals except for Hg, the concentrations of which were about five times higher than those observed in the high SO_3 mixes. Cd, Cu, and Hg were the heavy metals present in SSFAs in the highest concentrations compared to concrete. The remaining heavy metals measured had concentrations similar to or lower than those of the concrete test samples. Heavy metal concentrations in SSFAs are dependent upon the type of coal burned and the scrubbing material used in each power plant.

Physical Properties. *Porosity and Permeability.* The SSFAs were three–four times more permeable than the concrete test samples. Mixes 6 and 7 were more porous and permeable than mixes 4 and 5 (Table II). The relationship between porosity and permeability is a direct function of the amount of Ca available for calcium aluminosilicate precipitation in the cementation process. This precipitation results in a reduction in porosity and permeability.

Compressive Strength. Compressive strength (Table III) of all the test samples increased significantly with curing time. After 30 days of curing, the SSFAs had a compressive strength of 25–75% of the reference concrete. After 5 months of curing, the compressive strengths of the SSFA samples were 1.2–3 times greater than those observed at the end of 30 days, while concrete increased fivefold.

Comprehensive strength of concrete and similar cementitious phases varies as a function of curing time, humidity, temperature, water content, and additive content (fly ash, lime, etc.). The observed differences in hardness are due to variations in the composition of the samples. In the case of concrete, for example, the hardening process continues for many months due to the slow reaction kinetics and hydration processes associated with the precipitation of calcium and iron aluminosilicate phases, which are the cementing bonds for concrete. The abundance of Ca available for such reactions in concrete accounts for its strength. Unreacted Ca in SSFAs, resulting from incomplete scrubbing and/or the addition of Ca compounds (i.e., lime) as stabilizing agents, react with the

Table III. Physical Stability of Test Samples

days cured	days in seawater	age of sample, days	compressive strength, psi[a]					rel surface hardness[b]				
			4	5	6	7	concrete	4	5	6	7	concrete
30	0	30	110	320	160	200	425	mid	high	low	mid	high
150	0	150	215	920	205	355	2160	high	high	mid	high	high
120	30[c]	150						low	mid	v. low	v. low	high
120	30[d]	150						low	mid	mid	high	high
120	30[e]	152	180	840		320	1780	high	high	mid	high	high
30	120[e]	152				310	1520				mid	high
120	0[f]	150				245	1650				mid	high

[a] The coefficient of variation for compressive strength values, based on three replicates of one mix type (mix 4), was 7%. [b] Relative surface hardnesses were based upon comparisons of the numerical values obtained by the abrasion test as outlined under Methodology. [c] Samples were tested immediately upon removal from the seawater. [d] Samples were allowed to dry for 3 h after removal from seawater before testing. [e] Samples were allowed to dry for 2 days after removal from seawater before testing. [f] These samples underwent 20 cycles of rapid freezing and thawing in air requiring 30 days.

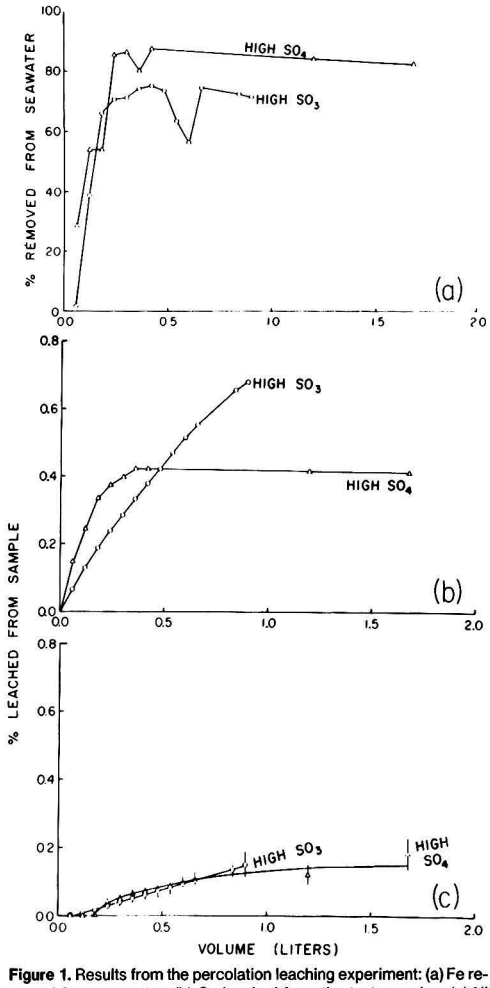

Figure 1. Results from the percolation leaching experiment: (a) Fe removed from seawater; (b) Cu leached from the test samples; (c) Ni leached from the test sample

added fly ash, which is rich in Fe and Si, to form calcium and iron aluminosilicates, as in concrete, through precipitation reactions (*13*). SSFAs contain less available Ca for reaction than concrete and therefore do not form as many strengthening precipitates as does concrete.

When SSFA and concrete test samples were immersed in seawater for 30 days, the compressive strengths of these samples were less than those values observed for samples cured an equal amount of time in humid air (Table III). The losses in strength for the SSFAs were 8–16% and the loss for concrete was 18%. Mix 7 (high in SO_4) and concrete were also subjected to 120 days immersion in seawater. Here it was found that mix 7 did not exhibit a significant reduction in strength beyond its 30-day loss. Concrete, however, lost an additional 12% of its initial strength beyond the 30-day loss. Variations in strength losses for SSFAs and concrete exposed to seawater may be due to different seawater attack processes occurring on the cementitious bonds. There are two principal processes by which seawater weakens cementitious bonds (*14*).

In the first process, loss of compressive strength can be attributed to sea salt intrusion into the block. Elevated pore water salt concentrations can cause migration of the water of hydration by osmotic processes, resulting in partial dehydration of cementation compounds and weakening of the solid structure. This process probably affects both SSFAs and concrete but is not as important as the second process in overall strength reduction over time.

In the second process sulfate ions in seawater react with one of the cementing phases in the blocks, namely, tricalcium aluminate ($3CaO{\cdot}Al_2O_3$) to form a precipitate, ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$) in situ, which occupies a 14% greater volume than the phase originally present. As this reaction occurs over time, concrete continually expands and subsequently loses its strength. SSFAs are probably not affected by this process to as great a degree as concrete, since they already contain very high concentrations of $CaSO_4$ resulting in high concentrations of SO_4 ions in the block's interstitial water. They also have high porosities that permit volume expansion with less internal pressures. Therefore, one would expect the compressive strength of SSFAs to be less affected over time by seawater than concrete, as was observed in this investigation and further ongoing marine in situ studies over an 18-month period (personal communication (*15*)).

Surface Hardness. All of the mix types, including concrete, exhibited continued surface hardening as curing proceeded (Table III). Immersion in seawater of the SSFA samples caused their surfaces to soften in varying degrees depending upon their compositions. Mixes 4 and 5, high in $CaSO_3$, softened slightly after 30 days exposure to seawater. Mixes 6 and 7, however, high in $CaSO_4$, showed more softening upon exposure to seawater. SSFAs containing high concentrations of $CaSO_4$ exhibited greater surface softening because of the greater solubility and higher dissolution rate of $CaSO_4$ as opposed to $CaSO_3$. When mix 7 was exposed to seawater for 120 days, it continued to soften on the surfaces, indicating that dissolution of the major soluble components continued to occur over extended periods of exposure to seawater. The degree of surface softening, however, was primarily superficial, indicating that the blocks were not readily losing their structural integrity in seawater. In contrast, concrete remained uniformly hard regardless of the exposure time to seawater, again demonstrating the difference in the processes involved for seawater attack on SSFAs and concrete.

Leaching Investigations. *Percolation Study.* The results of the percolation experiment are presented in Figures 1–3. $\Sigma a_n/A_0 \times 100$ is plotted as a function of V_n (*16*), where A_0 is the initial mass of component a_n present in the test sample, Σa_n is the cumulative mass of a_n that is leached from the test sample, $\Sigma a_n/A_0 \times 100$ is the cumulative percentage of a_n that is leached from the sample, and V_n is the volume of seawater percolated through the test sample.

With respect to minor component leaching, the results of the percolation experiment show that the heavy metals Fe, Cu, and Ni leached very little or not at all from the test samples during the time period of this experiment. Fe (Figure 1a) did not leach from the SSFA samples at all, but instead was absorbed from the percolating seawater by the test samples. Up to 85% of the Fe in the original seawater was removed. On the other hand, Cu (Figure 1b) leached from the samples initially but then reached equilibrium with the percolating seawater within the first 1.5 L of seawater percolation (based on a curve-fitting prediction for mix 5). As a result, less than 1% of the total Cu initially present in the SSFA samples was released by the samples. Ni leaching followed a similar pattern (Figure 1c), but the total release of Ni from the test samples was considerably less than that for Cu.

The leaching behaviors of Fe, Cu, and Ni appear to be interrelated and dependent upon the Eh of the percolating seawater. In the pH–Eh ranges encountered in this experiment (Figures 2a and b), the speciation (*17*) of these heavy

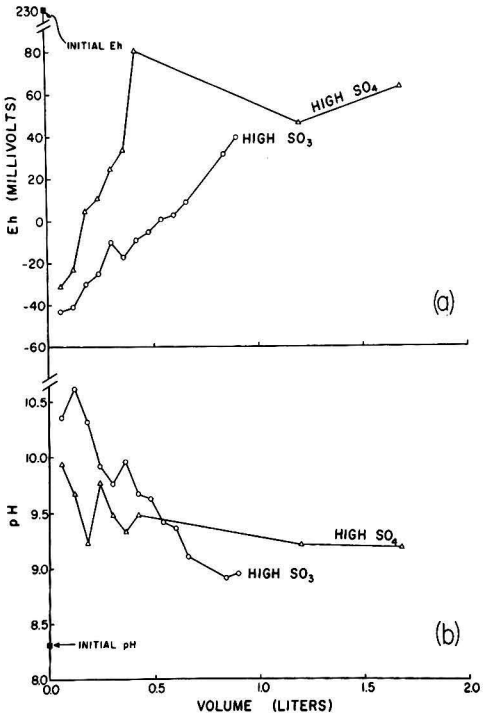

Figure 2. Eh (a) and pH (b) of seawater percolating through test samples of stabilized scrubber sludge and fly ash

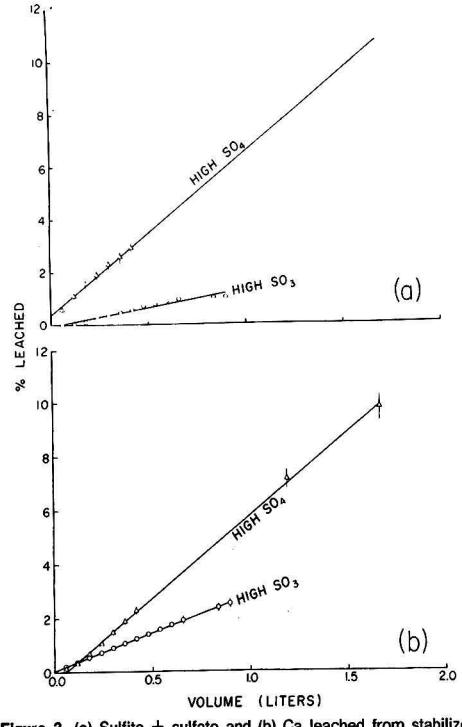

Figure 3. (a) Sulfite + sulfate and (b) Ca leached from stabilized scrubber sludge and fly ash during percolation

metals in seawater can account for the observed leaching behaviors. As percolation began, seawater Eh was drastically lowered due to the oxygen demand caused by $CaSO_3$. As more seawater percolated through the SSFAs, the oxygen demand decreased and therefore the Eh increased. In contrast, pH was highest during early percolation due to the dissolution of lime and subsequently decreased as lime leaching decreased. Cu and Ni release from the samples was at a maximum during the lowest Eh conditions, when Fe loss from the seawater was at a minimum. As the Eh increased, Fe loss from seawater increased probably due to the formation of insoluble Fe oxides in the seawater that adsorbed on the internal surfaces of the SSFAs. Additionally, Cu and Ni release from the SSFAs, which was facilitated by low Eh conditions, decreased as the Eh of the percolating seawater increased. This may be due to a coprecipitation or adsorption of Cu and Ni with the Fe oxides, which are known to be scavengers in seawater (*18*).

Leaching of the major components Ca and sulfur oxides (SO_3 and SO_4) was found to be relatively constant and rapid compared to the minor components (Figure 3).

Variations in the concentrations and solubilities of the Ca-containing compounds present in the different SSFA mixes can account for the observed differences in the leaching rates of Ca and sulfur oxides. The major Ca salts present in SSFAs are $CaSO_3$, $CaSO_4$, $CaCO_3$, and $Ca(OH)_2$. The resistance to leaching of the soluble Ca compounds in mix 5 can be explained by higher concentrations of less soluble compounds such as $CaCO_3$ and $CaSO_3$ found in mix 5. In mix 7, however, there are higher concentrations of the more soluble $CaSO_4$ than in mix 5.

Tank Study. Figure 4 shows the concentrations of dissolved Fe, Cu, and Ni in seawater containing the SSFA samples as a function of time. There was an initial increase of dissolved Fe and Ni within the first few days after exposure to seawater,

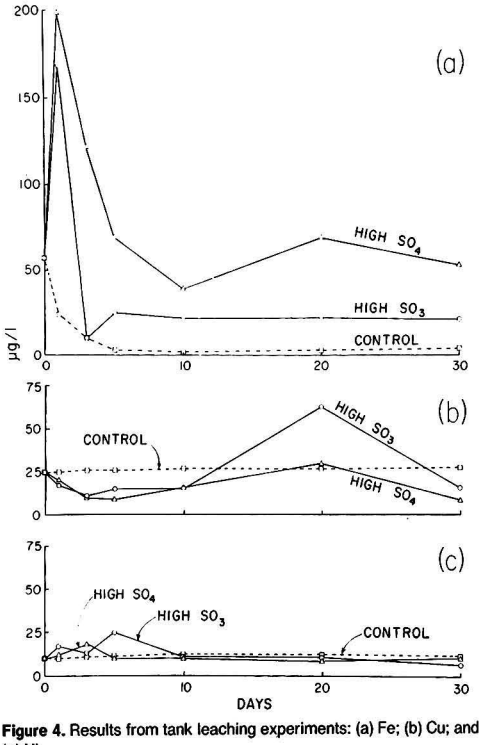

Figure 4. Results from tank leaching experiments: (a) Fe; (b) Cu; and (c) Ni

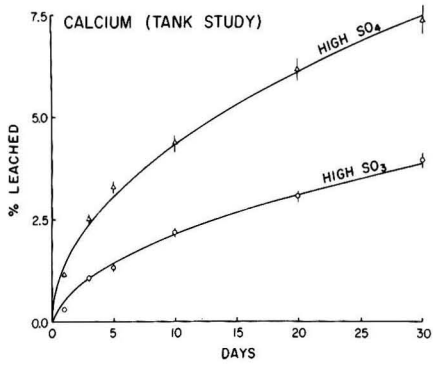

Figure 5. Release of Ca during the tank leaching experiment

but after approximately 10 days the concentrations of these components decreased to levels near the original seawater concentrations. The observed increase and subsequent decrease in dissolved Fe, Cu, and Ni concentrations are probably due to desorption–adsorption processes or precipitation reactions occurring on the surfaces of the SSFA and the suspended particulates that were released.

Concentrations of dissolved SO_3 observed during the tank study never exceeded 2 mg/L. Thus, stabilization of SSFAs significantly reduced the amount of $CaSO_3$ available for dissolution. Therefore, any SO_3 released would be rapidly oxidized to SO_4 in an aerobic environment. In an anaerobic environment dissolved SO_3 concentrations would be expected to increase.

The concentrations of Ca (and also SO_4) in the seawater steadily increased with time (Figure 5). As in the percolation leaching experiment, mix 7 was found to release Ca at a greater rate than mix 5. This is primarily due to a higher content of the more soluble Ca compound, i.e., $CaSO_4$ in mix 7 compared to mix 5, which contains greater concentrations of the less soluble $CaSO_3$ and $CaCO_3$.

The release of soluble components from the blocks occurs primarily on the outer surfaces as the permeabilities (Table II) of the SSFAs blocks are relatively low. This is evident from the much lower pH and Eh changes observed for the seawater in the tank experiment (Figure 6) compared to the percolation experiment (Figure 2). Therefore, it would be expected that the rate of leaching from blocks of SSFAs would be a direct function of the surface:volume ratio in static pressure environments such as the ocean.

Conclusions

The following conclusions demonstrate the advantages of stabilization as a means of minimizing the environmental impact imposed by the disposal of scrubber wastes and fly ash in the ocean:

- Stabilization of scrubber sludges and fly ash minimizes the rapid mobilization and dissolution of the minor components present.
- Leaching of the major calcium containing compounds is primarily regulated by their concentrations in the blocks, their solubilities, and the effective surface area:volume ratio of the blocks.
- The results suggest that blocks of SSFAs could remain stable in the ocean as an artificial reef for extended periods of time provided that organism colonization does not substantially reduce their structural integrity.

These conclusions are limited to the sample mixes used in this investigation. Variations in the components and their proportions in SSFAs due to the mix design, the characteristics of the scrubber process, the type of coal burned, and the stabilizing additives used could affect the behavior of SSFAs in seawater.

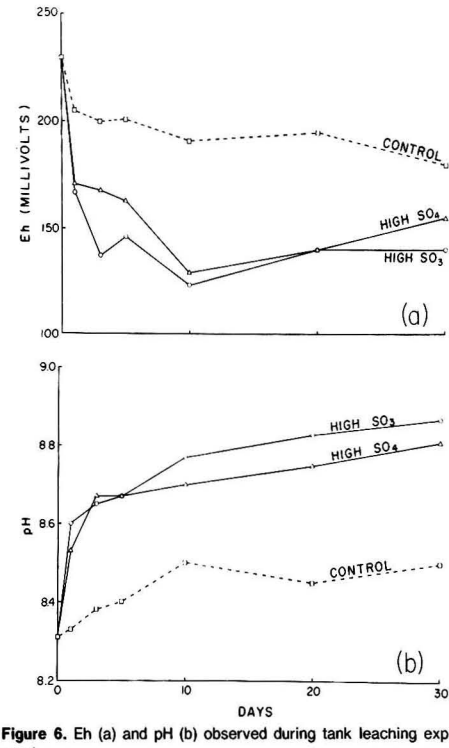

Figure 6. Eh (a) and pH (b) observed during tank leaching experiment

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Development of Long-Term Sulfur Dioxide Monitor Using Permeation Sampling

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■ A method has been developed for monitoring integrated or time-weighted-average sulfur dioxide concentration for time periods of weeks or even months. The approach is based upon the quantitative permeation of gaseous sulfur dioxide through a dimethylsilicone polymer membrane into a manganese salt solution, which subsequently stabilizes the collected sulfur dioxide by catalytic oxidation to sulfuric acid. Like the lead peroxide candle method, the permeation procedure does not require the use of pumps or motors and the product is photochemically and thermally stable. However, unlike the lead peroxide candle, which produces only relative SO_2-sulfation effect measurements, the newly developed method provides absolute quantitation in terms of concentration and is sulfur dioxide specific, humidity independent, and functional over a wide temperature range. The detection limit is 10 $\mu g/m^3$ for a 7-day exposure period. Exposure periods as great as 3 months are possible.

Sulfur dioxide has long been recognized as an important parameter in the determination and control of ambient air quality. In the past, lead peroxide candles (*1*) and Huey plates (*2*) have been used for monitoring sulfation effects. These devices, either Mason jars or petri dishes, respectively, when coated with a lead dioxide paste can be used to collect sulfur dioxide in the form of lead sulfate. This tedious method is generally unacceptable due to extraneous factors which affect the method's reliability. A lack of specificity, due to interferences by sulfate-containing aerosols, as well as humidity and wind velocity effects on the sulfation rate detract significantly from the usefulness of these methods (*3, 4*). More critical is the fact that sulfation rates are not quantitatively related to the ambient concentrations of sulfur dioxide.

More recent developments in technology involving the collection and determination of sulfur dioxide, incorporating permeation sampling techniques developed by Reiszner and West (*5*), now provide a valid approach for long-term sulfur dioxide monitoring. The stabilization of sulfur dioxide in the form of dichlorosulfitomercurate(II) for up to about 7 days is possible, but thermal and photochemical decomposition of the sulfito complex precludes the use of this approach for more extended periods. A better method is now proposed that is capable of monitoring sulfur dioxide for weeks or possibly months and does not require the use of electricity or complicated peripheral equipment. The results provide integrated values for ambient sulfur dioxide concentrations and can therefore be directly correlated to federal regulations. The method involves collecting sulfur dioxide by permeation of the gas through a membrane into a catalytic oxidizing solution, which stabilizes the sulfur dioxide as sulfate. The resulting sulfate sample is then analyzed turbidimetrically by precipitation as 2-perimidinylammonium sulfate.

[1] Deceased, March 1979.

Experimental

Apparatus. A Beckman DB spectrophotometer was used for absorbance measurements and an Orion Model 801 PH meter was used for pH determinations.

Reagents. All solutions were prepared in distilled, deionized water using only reagent grade chemicals.

Manganese(II) Chloride Solution. The manganese absorber solution was prepared by dissolving 3.6 g of manganese chloride tetrahydrate (Baker, Analyzed Reagent) in 650 mL of water. This solution was then diluted to 1 L with certified ACS grade glycerol and mixed thoroughly.

2-Perimidinylammonium Bromide (PDA-Br). PDA-Br is not commercially available at this time and, therefore, was prepared in the laboratory. The first report of 2-perimidinylammonium ion used as an analytical reagent for the turbidimetric measurement of sulfate was suggested by Stephen (*6*). Dasgupta et al. (*7*) have recently improved the synthesis of PDA, increasing the percentage yield and purity of the product. A 0.5% solution of PDA-Br reagent was prepared by dissolving 0.5 g of PDA-Br in 100 mL of water by gently heating. The resulting filtered solution provided enough reagent for 25 sulfate determinations, according to the recommended procedure. This solution was prepared daily.

Sulfate Standards. For stock standards, sulfuric acid was diluted to approximately 0.02 N and standardized against a sodium hydroxide solution that had been standardized against primary standard potassium hydrogen phthalate. This solution, containing 960 mg per mL of sulfate, was then diluted to produce working standards.

Preparation and Calibration of Permeation Monitors. An abbreviated summary of the procedure for the preparation and calibration of the permeation device, developed by Reiszner and West, is presented here. Each permeation device was prepared by sealing a single-backed dimethylsilicone rubber membrane, available from General Electric Co. (Schenectady, N.Y.), to one end of an 8 cm column of 41 mm o.d. glass tubing using silicone rubber cement. The opposite end of the device was fitted with a no. 8 neoprene rubber stopper and capillary tube. The capillary tube eliminated any pressure gradient which might damage the polymer membrane. Six milliliters of manganese absorber solution was added to each device and exposed to a known concentration of sulfur dioxide for given periods of time. The calibration

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Table I. Absorber Efficiencies

absorber (1000 ppm)	effective time, min at >90% effic
$Co(NO_3)_2$	30
$Ni(NO_3)_2$	20
$Mg(NO_3)_2$	20
$Cu(NO_3)_2$	24
$Hg(NO_3)_2$	>240
$Fe(NO_3)_3$	>240
$Cr(NO_3)_3$	240
$Zn(C_2H_3O_2)_2$	260
$Ce(NO_3)_3$	300
$MnCl_2$	300
Na_2HgCl_4 (0.1 M)	98

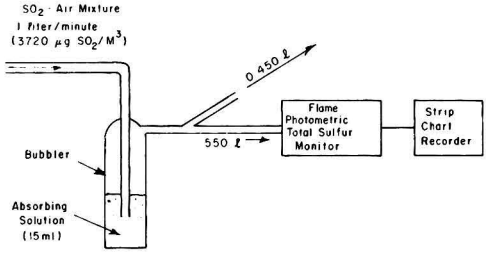

Figure 1. Apparatus for measuring absorber efficiency

constants were then calculated from the following equation:

$$k = \frac{Ct}{w}$$

where k = constant, usually on the order of 10^3 h/m^3, C = concentration of sulfur dioxide, μg/m^3, t = time, h, and w = amount of sulfur dioxide absorbed, μg. Utilizing the technique developed by O'Keeffe and Ortman (*8*), standard sulfur dioxide–air mixtures were prepared by purging known amounts of charcoal-filtered, dried air over a standard sulfur dioxide source. These known concentrations of sulfur dioxide were then used to expose permeation monitors for calibration purposes.

Sampling. The permeation devices used for sampling ambient sulfur dioxide were first charged with 6 mL of manganese chloride absorber solution and then exposed to the sulfur dioxide/air mixtures. The exposure times were typically 5 to 6 days for the detection of 10 μg/m^3 of sulfur dioxide. Any anticipated decrease in absorber volume due to evaporation was made up with deionized water before starting the exposure. Experimental results indicated average losses of 0.5 mL per day in the field at average temperatures of 30 °C. An initial charge of 6 mL of manganese solution plus 10 mL of deionized water was found to be adequate for a normal 30-day sampling period in the Louisiana area during the summer. Up to 50 mL of water may be added; however, the volume to be analyzed must not exceed 6 mL. The unrestricted movement of air over the membrane was found to be essential and therefore the monitors were positioned in a manner which left the membrane unobstructed.

Analysis. The total sample volume was adjusted to 6 mL either by dilution or evaporation. To this sample volume, 4 mL of freshly prepared 0.5% PDA-Br solution was added and the mixture was then agitated thoroughly. The samples were allowed to nucleate for 10 min and the absorbance was then measured at 420 nm using a 3-cm glass cuvette. Blanks of

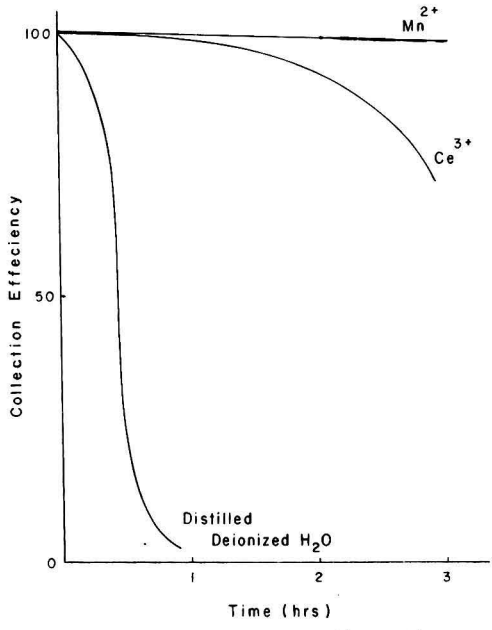

Figure 2. Collection efficiency of 10 ppm of Ce^{3+} and Mn^{2+} solutions

approximately 0.01 absorbance relative to water were obtained if the PDA-Br reagent was of acceptable quality. The absorbance at 420 nm after 10 min was linearly proportional to the amount of sulfate in solution. The total weight (w) of sulfur dioxide oxidized to sulfuric acid was calculated by preparing an absorbance vs. concentration curve to determine the sulfate content, which was then expressed in terms of micrograms of sulfur dioxide absorbed. The average time-weighted concentration, C, of sulfur dioxide in air for the sampling time, t, was calculated using the equation:

$$C = \frac{wk}{t}$$

Results and Discussion

Selection of Absorber Reagent. The catalytic oxidation of gaseous sulfur dioxide by aqueous solutions of manganese salts was independently investigated by Vasilev et al. (*9*) and Grodzovski (*10*) in the same year. Bassett and Parker (*11*). found that among several metal salts and oxides that were catalytic by nature, manganese was the most efficient studied. Also, it was found that the amount of dithionic acid formed by catalytic oxidation with manganese salts was negligible, unlike the case with many other salts. Working with unbuffered aqueous solutions, we confirmed and extended these studies to include additional salts. By bubbling a 3720-μg/m^3 sulfur dioxide–air mixture through 15-mL volumes of each salt solution at a rate of 1.0 L/min, and monitoring the resulting sulfur dioxide exhaust with a Bendix Model 8300 flame photometric total sulfur monitor, a table of relative absorber efficiencies was prepared (Table I and Figure 1).

Mercuric nitrate was considered to be inferior to either manganese(II) chloride or cerium(III) nitrate due to the inherent toxicity of the solution. Also, iron(III) nitrate was discounted on the basis of colorimetric interference. A comparison of $Ce(NO_3)_3$ and $MnCl_2$ absorber efficiencies at cation concentrations of 1000 ppm indicated no significant differences. However, by making absorber dilutions, it was possible to determine the most efficient reagent because the rate of the

oxidation reaction is dependent on catalyst concentration. By evaluating each absorber at 10 ppm, $MnCl_2$ was selected as the best absorber reagent (Figure 2).

As one might expect, there is a marked effect of pH on the rate of the oxidation reaction (e.g., the reaction is favored by a neutral or alkaline pH). Formation of sulfuric acid slows the oxidation rate until eventually a steady state is achieved. The rate patterns for manganese(II) chloride aerosols were described by Matteson et al. (*12*). Values reported for the H_2SO_4 concentration at which the oxidation approached a steady state varied between 20 and 40 wt %. Using the above reported literature, and absorber efficiency information reported here, the sulfur dioxide absorber concentration was chosen to be 1000 ppm of manganese in aqueous solution. It has a large excess absorbing capacity and concentrations higher than this would cause precipitation of PDA-Cl during the subsequent analysis.

Certified ACS grade glycerol was added to the absorber solution, providing a 41% by weight glycerol solution. The freezing point of the absorber solution was thus reduced to approximately −16 °C. The reduced freezing point of the absorber solution made sampling operations possible over an extended temperature range. Also, the glycerol served a secondary purpose by increasing the viscosity of the sample solution, acting effectively as a suspending agent for the turbidimetric determination of sulfate. The apparent pH of the absorber solution was 4.8. A repeat of the absorber efficiency study indicated a decrease in capacity of the absorber after addition of the glycerol. However, the capacity was felt to be far in excess of what is needed for a permeation method.

Temperature Effect. The effect of temperature on the permeability of the dimethylsilicone rubber membrane was studied over a temperature range of 50 °C. The results, when expressed as a linear plot of mean percent difference in the reciprocal permeation rates vs. temperature, indicated that the calibration constant k decreased 6.3% per 10 °C increase (Figure 3). This phenomenon was assumed to be due to changes in the mass transfer rate through the silicon rubber membrane, rather than kinetic effects on the rate of oxidation of sulfur dioxide to sulfate. This conclusion was supported by earlier work done by Reiszner and West, illustrating similar temperature effects on the permeation rates of sulfur dioxide in dimethylsilicone rubber using sodium tetrachloromercurate as the absorber–stabilizer (*1*).

Humidity Effect. All experiments were conducted at approximately 30% relative humidity, to avoid repeating the work previously reported that demonstrated the permeability of sulfur dioxide in silicon rubber membranes of this type to be constant over a range of 0–90% relative humidity. Even condensation of moisture on the membrane failed to affect the permeation rate.

Response Time. Because the permeation of gases through polymer films is not an instantaneous process, the time between the initial exposure of the device to sulfur dioxide and the subsequent dissolution, permeation, and evolution of sulfur dioxide to the opposite side of the membrane must be quantified. This lag time has been studied by Reiszner and West (*5*) and termed insignificant in relation to long-term exposures. The permeation rate for the silicone membrane attains 90% of the steady-state value within 10 min of exposure. However, brief pulses of sulfur dioxide of less than 10-min duration are quantitatively integrated provided the sampling is continued at least 2 min beyond the pulse.

Influence of Sulfur Dioxide Concentration on Permeability. The calibration constant values were measured at concentrations of 660 to 1975 $\mu g/m^3$ (Table II). The percentage deviation from the mean k value was <5% at 23 °C, indicating that the k value was independent of sulfur dioxide concentrations, as was reported earlier (*1*).

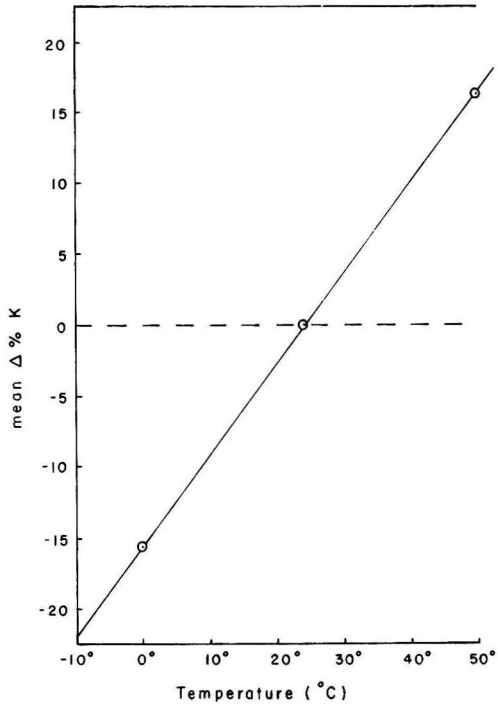

Figure 3. Effect of temperature on rate of permeation

Table II. Effect of Concentration on Calibration Constant

device no.	k, h/m³ at 660 μg/m³	k, h/m³ at 1975 μg/m³	% deviation
1	1299	1346	3.6
2	1246	1224	1.8
3	1442	1427	1.0
4	1356	1291	4.7
5	1418	1346	5.2

Interference Study. Only gaseous sulfur compounds, which could permeate through the membrane and lead to insoluble PDA salt-forming species, could conceivably interfere with the determination. Therefore, the interference study was restricted to the evaluation of hydrogen sulfide effects on the measurement of sulfur dioxide. The aftereffect of hydrogen sulfide exposure was studied to determine what physical damage might be incurred by the polymer membrane, as well as any positive interferences due to oxidation of hydrogen sulfide to sulfuric acid.

A battery of five permeation monitors charged with 5 mL of manganese absorber was exposed to hydrogen sulfide (4500 μg of H_2S per m^3) for a period of 16.5 h at 24 °C and a relative humidity of 30%.

The results obtained from the turbidimetric analysis of the absorber solutions indicated no interference due to the oxidation of hydrogen sulfide. The question of whether the hydrogen sulfide permeated across the membrane under these conditions remains unanswered. Current research indicates that the permeability of hydrogen sulfide is extremely humidity dependent and that relative humidity and permeability are inversely related (*13*). Evaluation of the sulfur dioxide calibration constants after the hydrogen sulfide exposure

indicated that the membranes had not suffered physical damage as in the previous permeation method (5).

Comparative West–Gaeke vs. Turbidimetric Evaluation. Using disodium tetrachloromercurate(II) as the absorber solution, the colorimetric West–Gaeke method for sulfur dioxide determination was used to determine the permeation monitor calibration constants. A set of duplicate calibration experiments was conducted to substantiate the previously determined sulfur dioxide permeation rates and illustrate the quantitative nature of the newly developed technique. The calibrations were made after an exposure of 3 h of 660 $\mu g/m^3$ of sulfur dioxide at 24 °C. The mean percentage deviation between the two methods of calibration was less than 2%. These results indicated essentially 100% of the sulfur dioxide that permeated into the manganese solution was converted to sulfuric acid at a rate rapid enough to avoid affecting the sulfur dioxide permeation constants.

A cursory feasibility study of the newly developed method was conducted in the field for a period of 1 month in parallel with a West–Gaeke bubbler assembly. The results obtained from both methods indicated that only rural background levels of sulfur dioxide were present (below 10 $\mu g/m^3$ of sulfur dioxide).

Conclusions

This research, which involved the development of the manganese(II) chloride procedure, was successful in producing a viable alternative to the 40-year old lead peroxide candle method. This work has demonstrated the high degree of quantitation achieved by the manganese method as opposed to the nonquantitative lead candle method.

The maximum possible exposure period, based upon the average evaporation loss of absorber solution under field conditions, was determined to be 3 months. The detection limit was established to be 10 $\mu g/m^3$ of sulfur dioxide for a 7-day exposure period. The blank absorbance value at 25 °C was 0.01 provided the PDA reagent was of acceptable quality. The absorbance vs. sulfate concentration calibration curve was linear over a range of 0.1–10 ppm. The absorber solution was nontoxic and therefore was handled with care to avoid contamination by biologically active organisms. The high stability of sulfuric acid in aqueous solutions enabled collected samples to be stored for extended periods of time in glass or polyethylene vials without decomposition or adsorption. The method was found to be specific for sulfur dioxide and independent of humidity effects over a range of at least 0–80% relative humidity. The effect of temperature on the rate of permeation of sulfur dioxide through the polymer membrane resulted in a 6% decrease in permeation for every 10 °C increase in temperature.

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A Personal Chlorine Monitor Utilizing Permeation Sampling

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■ A method for the determination of personal exposure to chlorine is described. Samples are collected by permeation through a silicone membrane into 10 mL of a fluorescein–bromide absorbing solution. The resulting eosin is measured spectrophotometrically and the Cl_2 exposure (time-weighted-average) is calculated. The detection limit of the method is 0.013 ppm (0.038 $\mu g/m^3$ at 20 °C) for an 8-h exposure with a working range of 0.1–2.0 ppm. The device responds in less than 1 min and is unaffected by variations of temperature and humidity. Response of the device is dependent on pH and is optimized by buffering the absorbing solution at pH 7.0. No significant interferences are encountered, but the solution fades if exposed to intense sunlight for extended periods. A device can be constructed that is small in weight and size and can serve as either an area or personal monitor.

Federal regulations have set the present personal exposure limit for chlorine at 1 ppm (8-h time-weighted-average) (*1*), emphasizing the need for monitoring methods that reflect actual individual exposures. Current procedures used to determine personal exposures to Cl_2 are active sampling methods in which the air sample is drawn through a liquid absorber. These involve the use of a pump, battery pack, and glass impinger. Two of the present approaches used for determining the collected Cl_2 involve the use of *o*-tolidine (*2*) or methyl orange (*3*). In the first, the sample is collected in NaOH and, at the end of the collection period, *o*-tolidine is added. A yellow color is produced and measured spectrophotometrically. The latter technique relies on a quantitative bleaching of a methyl orange solution, which is also determined spectrophotometrically. The color developed in the *o*-tolidine method is unstable, and the reaction itself is acutely dependent on pH (*4*). The methyl orange method, like all other bleaching methods, lacks precision and accuracy at low chlorine concentrations.

The relatively bulky, inconvenient, and expensive collection devices now available are a deterrent to personal monitoring.

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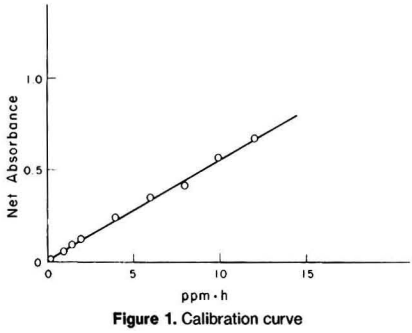

Figure 1. Calibration curve

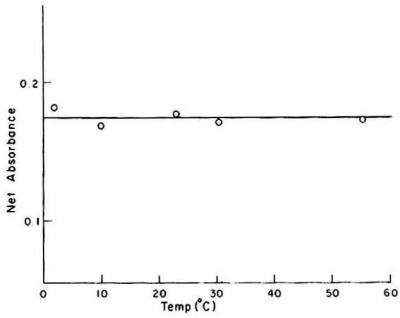

Figure 2. Effect of temperature on permeation

The problems of the mechanical and chemical processes involved add further to the need for a better approach for personal monitoring for chlorine.

A new method is proposed which is low in cost and simple to use. It may be employed for sampling periods as short as 30 min or as long as 12 h. The new method utilizes a permeable membrane for sample collection, where the permeation rate is proportional to the external Cl_2 concentration (*5*). Samples are collected directly into a color developing solution, which has proven to be stable over long periods of time. At the end of exposure, the solution is transferred to a cuvette and measured spectrophotometrically.

The absorbing solution consists of a fluorescein–bromide mixture in which Cl_2 oxidizes bromide to bromine, which in turn brominates fluorescein (*6, 7*) to form eosin, which is then measured at its absorption maximum, 519 nm. The detection limit for this method is 0.013 ppm of Cl_2 for an 8-h exposure, with a working range of 0.1–2.0 ppm. For shorter periods of time, concentrations as high as 5 ppm can be accurately measured.

Experimental

Reagents. High-quality distilled, deionized water was used throughout. All reagents were reagent grade where possible. Fluorescein (no. P780, 96% assay, Eastman Kodak Co.) was obtained in acid form, and eosin (no. E-511, 87% assay, Fisher Scientific Co.) was obtained as the disodium salt.

A fluorescein stock solution was prepared by dissolving the following in deionized water and diluting to 2 L: 0.011 g of fluorescein, 6.19 g of NaBr, 2.24 g of NaOH, 13.6 g of KH_2PO_4. The fluorescein and NaOH were added first with a few milliliters of water, and the mixture was then agitated vigorously to convert the fluorescein to its sodium salt (uranin), thus increasing its solubility. The resulting solution was 16 μM fluorescein–0.03 M NaBr with a pH buffered at 7.0.

The reagent is slightly light sensitive but may be stored in the dark for at least 1 month without significant alteration. Naturally, it must be protected from direct exposure to sunlight when used in a personal monitor. Decomposition does not change the linearity of the method but the range decreases with decomposition of fluorescein. High blanks are an indication of Cl_2 in the water or decomposed reagents. Low blanks are an indication of impure fluorescein or decomposition of the reagent due to exposure to sunlight. The blank absorbance vs. water, typical of our studies, was 0.029.

Apparatus. The calibration chamber, permeation devices, gas filtration and dilution system, and other auxiliary equipment have been described by Reiszner and West (*5*). The permeation devices used in this study employed General Electric single-backed dimethylsilicone membranes of 0.025 mm thickness.

Calibration of Permeation Devices. Standard Cl_2–air mixtures were prepared by passing dry filtered air over a standard permeation tube (*8, 9*), which emitted Cl_2 at a constant rate. A 10-mL aliquot of the fluorescein solution was pipetted into the permeation device, which in turn was placed in the calibration chamber. The solution was transferred into a cuvette at the end of the exposure period, and the absorbance measured at 519 nm with the original fluorescein solution taken as blank. The calibration constant (K) of each device was calculated by exposing the monitor to a known concentration of Cl_2 for a measured period of time. This constant is defined as:

$$K = A/(Ct) \quad (1)$$

where K = constant, absorbance units/(ppm·h), t = exposure time, h, C = Cl_2 concentration, ppm, and A = measured absorbance at 519 nm with a 1-cm cell. The constant, K, is the reciprocal of the constant k, as defined in the original theory on permeation sampling (*5*).

A linear response to cumulative dosage was verified by determining the absorbance after exposure to various Cl_2 concentrations and exposure periods. The results are shown in Figure 1. The devices used in this study had K values of about 0.05 absorbance unit/(ppm·h) or, in absolute units, 0.56 μg of Cl_2/(ppm·h). Although membrane thickness and exposed surface area can be varied to alter sensitivity, changes should be made only with caution.

Analysis. It is imperative that the analysis procedure be the same as that used for calibration. Then, by exposing the device for a known length of time, the following equation can be used to find the average time-weighted Cl_2 exposure:

$$C(\text{ppm of } Cl_2) = A/(Kt) \quad (2)$$

where K is the constant as defined in Equation 1.

Results and Discussion

Effect of Temperature. Because calibration of the devices was done at 24 °C, it was necessary to determine if changes in temperature would cause any deviation in response. The effects of temperature were studied over a range of 0–55 °C. As illustrated in Figure 2, no significant deviations in response were observed.

Effect of Humidity. A dry air stream was used for calibration, and it was felt that some deviations in permeation may occur at higher relative humidities (RH). Humidity was varied by mixing a humid air stream with the dry Cl_2–air stream coming from the permeation chamber. The humid stream was produced by directing air flow through two impingers, the first containing water and the second left empty to serve as a condensation trap. By varying the water level and temperature of the first impinger, it was possible to vary the humidity without changing the flow-meter settings. All RH measurements were made in the exposure chamber with a solid state probe. Over a range of 0–97% RH, response remained unaffected.

Table I. Response Time

time, min[a]	absorbance, 519 nm
0	0
3	0.013
6	0.013
9	0.013
12	0.012

[a] This represents elapsed time; the solution in the monitor was changed at 3-min intervals.

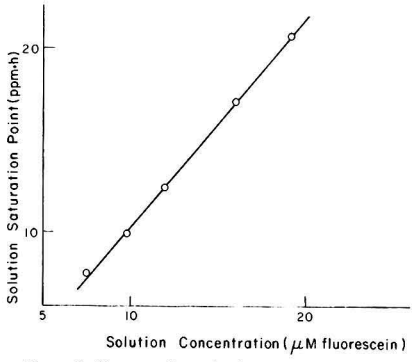

Figure 3. Cl_2 saturation point for absorber solutions

Response Time. Permeation through a membrane is not an instantaneous process. With some membranes, the response may take several hours (*5*). In an industrial environment, the device may be subjected to brief periods of high Cl_2 concentrations and it is important that it responds quickly. By exchanging the solution at 3-min intervals in a device being exposed to a Cl_2 stream, response was found to be 100% within the first 3 min (Table I). This places the response time at less than 3 min, and the actual value probably is less than 0.5 min.

Effect of Absorber Concentration. While fluorescein does not absorb very strongly at 519 nm, the variation of the blank at this wavelength could be significant when low concentrations of Cl_2 are to be determined and high fluorescein concentrations are used. For this reason it was desirable to keep the fluorescein concentration as low as possible, bearing in mind the amount of eosin formed is independent of the fluorescein concentration, unless the latter becomes the limiting reagent. On the other hand, the use of too dilute an absorber solution would result in rapid saturation leading to the bleaching of the product. The lower limit of the absorber concentration was dictated by the upper limit of the cumulative exposure to be measured. After a study of various absorber concentrations (Figure 3), it was found that a 16 μM solution of fluorescein was the optimum choice for measuring 0.8–16 ppm·h of Cl_2 exposures in the devices being studied. If higher Cl_2 levels are anticipated, the fluorescein concentration can be increased.

Experience has shown that the permeability of different batches of membrane varies widely. The concentration of fluorescein must be increased in proportion to any increase in permeability if the range of the method is to be maintained. Calibrations must be carried out with the same reagent that is used in the field exposure. Dilution of the reagent after exposure may be necessary to obtain on scale readings.

Anticipating the use of a personal chlorine monitor under a wide variety of lighting conditions, an evaluation of the effect of light on the absorbing reagent was undertaken. The fact that bromide ion is light sensitive would lead one to expect a positive response to sunlight. Fortunately, no positive response was noted even after exposure for about 4 h to intense direct sunlight. The fluorescein color (absorbance at 490 nm) did fade almost completely during this exposure and the absorbance of the solution was slightly below that of the blank. This intense fading was reduced to about 50% in a prototype personal monitor, with all areas except the membrane face protected during a 4-h exposure. Eosin, which is formed from exposure to chlorine, also fades but at a reduced rate, which means that the primary concern must be with the fluorescein itself.

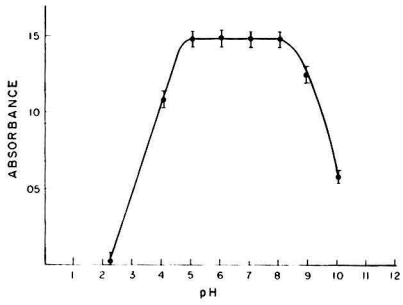

Figure 4. Effect of pH on response

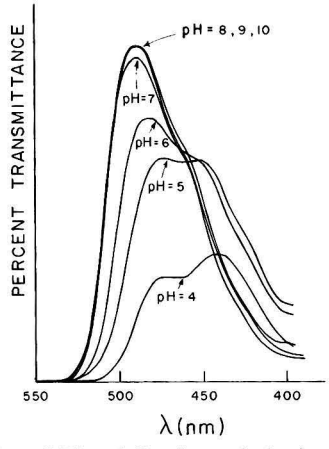

Figure 5. Effect of pH on fluorescein absorbance

Effects of pH. The effects of pH of the absorber solution were studied to determine the region of optimum response. Buffered adsorber solutions at pH 5, 6, 7, 8, 9, and 10 were studied. It was found that solutions with pH in the range 5–8 resulted in the greatest conversion of fluorescein to eosin (Figure 4). Solutions with pH values less than 5 resulted in the formation of a precipitate where solutions with pH >8 resulted in reduced eosin production. Buffering of the absorber solution to pH 7 was chosen to assure optimum eosin formation without the risk of precipitation. It was also noted that while the λ_{max} for fluorescein was pH dependent, the λ_{max} for eosin remained constant over the entire pH range studied (Figures 5 and 6).

Evaporation Study. To compensate for possible evaporation losses, the initial studies were conducted by diluting both the sample and blank to 25 mL with deionized water. Later studies indicated that less than 3.5% evaporation loss occurred when one of the devices that contained 10 mL of the absorber solution was exposed for 8 h to completely dry air at

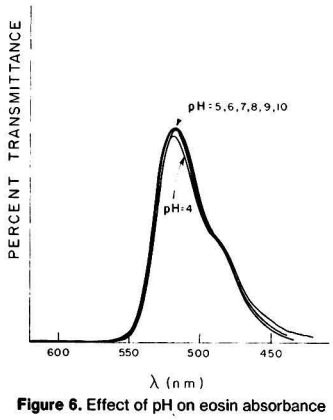

Figure 6. Effect of pH on eosin absorbance

24 °C. Therefore, all further studies were conducted without efforts to compensate for the evaporation loss. It should be pointed out that the evaporation loss will increase with elevated temperature, and quantitative transfer and dilution may be necessary if high degrees of accuracy are desired.

Interferences. Only gaseous pollutants can conceivably interfere with the permeation process. Furthermore, in order to cause an interference, the interferent would logically be an oxidant that would convert bromide to bromine or react with fluorescein or eosin directly. Ozone and nitrogen dioxide were therefore expected to have some effect. Nitrogen dioxide, with an exposure limit of 5 ppm (*1*), could conceivably present a serious problem. By exposing the devices to 5 ppm of NO_2 for 6 h, it was found that the response was only +0.01% of an equivalent Cl_2 exposure. While the exposure limit to ozone, 0.08 ppm (*1*), is well below that of Cl_2, even low O_3 levels might cause significant errors at low Cl_2 concentrations. Devices exposed to 5 ppm of O_3 for 4 h produced no measurable response. Therefore, neither NO_2 nor O_3 represent significant interferences. During field tests of the monitor, an inadvertent loss of hydrogen chloride occurred. The monitor seemed unaffected, but laboratory studies were undertaken which confirmed that exposure to 1500 ppm·h of HCl was without effect.

Field Tests. Independent field testing was conducted at a local chlorine production facility. Five calibrated Cl_2 monitors and a supply of the reagent were furnished for testing. At the discretion of the plant personnel, replicate samples were taken with the monitors and with battery-operated pump with impinger samplers placed in areas of the plant considered to represent typical exposures. Monitoring was conducted for 2-h periods with the subsequent analysis being done by the plant personnel. Data so observed are shown in Table II.

Table II. Field Evaluation

date	impinger, ppm of Cl_2[a]	permeation device, ppm of Cl_2		
12/1/78	0.47	0.52	0.67	0.56
	1.10	1.10	1.20	
	0.28	0.44	0.49	0.52
12/4/78	0.80	0.80	0.90	0.90
	0.90	0.70	0.60	
12/5/78	0.04	0.25	0.28	0.26
	0.03	0.16	0.22	
12/6/78	0.09	0.40	0.20	0.30
	0.09	0.20	0.20	
12/6/78	0.20	0.20	0.20	0.10
	0.20	0.20	0.20	
12/7/78	0.93	0.97	1.10	1.10
	0.93	0.95	0.97	

[a] Determination made by modification of methyl orange method (*10*).

Conclusion

The results reported here show that the measurement of Cl_2 can be accomplished in a simple yet efficient manner by using a technique that allows direct conversion of chlorine to a measurable product. Of special importance are the small size and convenience of the monitoring device employed.

The complete personal monitor for chlorine is a passive device the size and weight of a radiation dosimeter that serves the dual function of quantitatively sampling and determining Cl_2. The device can serve for personal or area monitoring or for ambient air studies.

Acknowledgment

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Smog Chamber Studies of Temperature Effects in Photochemical Smog

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■ Irradiations of selected hydrocarbon–NO_x–air mixtures were carried out over the temperature range −3 to 60 °C in a 5800-L, thermostated evacuable environmental chamber. The federal air quality standard for ozone, 0.08 ppm (1-h average), was exceeded within 6 h of irradiation of a surrogate hydrocarbon–NO_x mixture approximating an urban atmosphere, even at 5 °C. In all three systems studied (propene, toluene, and surrogate), rates of ozone formation increased significantly with temperature. In propene–NO_x–air and in toluene–NO_x–air reaction mixtures, the amounts of hydrocarbon consumed and the approximate amounts of NO to NO_2 conversion increased significantly with temperature. The nature of the O_3 concentration–time profiles in high concentration propene–NO_x experiments was significantly affected by temperature. In runs between 11 and 33 °C, $[O_3]$ peaked slightly before most of the initially present NO_x was consumed as is usually the case. However, for $T \leq 11$ °C, $[O_3]$ peaked significantly earlier and, for $T \geq 33$ °C, significantly later than the time of NO_x consumption. Furthermore, in a run at $T \simeq 50$ °C, $[O_3]$ reached a maximum prior to complete NO_x consumption, then decreased slightly, and finally slowly increased to a second maximum. The mechanistic implications of these observations are discussed.

It is well known that the formation of photochemical smog is influenced by a number of meteorological factors (*1–5*). Their natural fluctuations contribute to the observed variation in the frequency and the intensity of episodes in different geographic locations and at different times of the year. Among the most important factors from a fundamental gas-phase chemical kinetic standpoint is temperature. Unfortunately, although recently there has been significant progress in understanding the temperature dependences of elementary processes, to date no quantitative experiments concerning the overall temperature dependence of ozone production have been conducted. Such information could be useful to control officials and to atmospheric scientists alike, for example in testing the validity of complex kinetic-computer models of photochemical air pollution as applied to "real world" situations where temperature extremes exist.

Previous studies concerning the effects of temperature on photochemical smog formation have been reviewed in the EPA air quality criteria documents for ozone and other photochemical oxidants (*2, 3*). It was concluded that both laboratory and field studies verify the existence of a significant, positive temperature effect. Additionally, on the basis of an analysis of field data (*4*), in which a good correlation between maximum 1-h oxidant levels and daily maximum temperatures was observed, and on the basis of outdoor smog chamber studies performed in the winter and summer (*3, 6*), it was suggested (*4, 7*) that "below a cutoff temperature of approximately 55–60° F (15 °C) atmospheric reactions are not fast enough to yield oxidant/ozone at levels above 0.08 ppm when pollutants react for 1 solar day."

Substantial effects of seasonal changes of light intensity, duration, and spectral characteristics were predicted in computer model calculations by Nieboer et al. (*8*) and Bottenheim et al. (*9*). Indeed, Bottenheim et al. (*9*) also calculated that the effect of seasonal variations of temperature on overall smog chemistry was minor. However, their model did not include PAN (*10, 11*) and peroxynitric acid (*12, 13*) decompositions, which are now known to be important and highly temperature dependent. Thus, it is highly probable that their model underpredicts temperature effects.

Direct evidence that significant photochemical smog formation can occur at low temperatures comes from ambient air measurements by the Colorado Department of Health (*14*). Over 0.2 ppm of O_3 was observed near Denver on a clear March day in which the temperature did not exceed 52 °F. These results contradict the conclusion in the Air Quality Criteria Document for Ozone cited above (*3*). Clearly, there is an important need for unambiguous data concerning the effect of temperature *alone* on photochemical smog formation.

Few data concerning temperature effects are available from smog chamber studies of photochemical air pollution, since such experiments have traditionally been conducted over a relatively narrow range of temperature, typically ~25–35 °C. This has resulted from the experimental complexities involved in accurate temperature regulation of the large environmental chambers required for such studies.

On the other hand, analysis of air quality and outdoor smog chamber data is not, unfortunately, an unambiguous method for determining temperature effects, since conditions of lower temperature are often also associated with conditions of reduced light intensity or duration, which of course has a significant impact on smog formation (*1–4, 8, 9*).

In order to address this problem, a 5800-L evacuable environmental chamber (*15, 16*) in our laboratories was designed and constructed with the capability for a wide range of temperature control (e.g., −20 to +100 °C). This capability already has been utilized in kinetic studies of the temperature-sensitive species peroxynitric acid (*12, 13*). This evacuable chamber–solar simulator facility is currently being used in a program to determine the effects of temperature and other physical parameters such as UV spectral distribution (*17*) on photochemical smog formation processes. In this paper three categories of hydrocarbons are treated: (a) mixtures designed to resemble as closely as possible the composition and concentration ranges occurring in a polluted urban airshed [in our studies, these consist of sub-parts per million concentrations of oxides of nitrogen (NO_x) and a "surrogate" hydrocarbon mixture consisting of 12 alkanes, olefins, and aromatics designed to represent hydrocarbon emissions from all sources in the Los Angeles air basin (*18*)]; (b) mixtures consisting of sub-parts per million concentrations of NO_x and the single hydrocarbons propene or toluene; (c) mixtures consisting of NO_x and propene in concentration ranges greater than ambient. Studies of high concentration systems are useful because chamber effects relating to unknown radical sources, known to be important in ambient concentration smog chamber studies (*19–21*), are minimized by increasing the relative importance of known homogeneous radical sources. This also allows tests of detailed models under a wider variety of conditions, and allows a larger number of trace intermediates and products to be detected.

Experimental

Experimental Facilities and Methods. The experimental facilities and methods employed in these smog chamber experiments are discussed in detail elsewhere (*15, 16, 22–24*) and are only briefly described here. The evacuable thermostated chamber (*15, 16*) consists of a 5800-L cylindrical aluminum alloy cell coated on the inside with Teflon and equipped with

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quartz end windows (UV cutoff ~200 nm). Photolyses were performed using a 25 000 W solar simulator (22) producing a collumated beam designed to minimize direct irradiation of the chamber walls. The light was filtered by a 0.25-in. Pyrex pane to cut off radiation below ~290 nm.

The temperature control system was designed to regulate the temperature of the chamber walls to ±0.5 °C over the −20 to +100 °C range. In this system ethylene glycol is heated or cooled by external heat exchangers and then circulated by means of a 1.5 hp pump through channels welded to the chamber exterior. A YSI Model 71A temperature controller diverts the circulating fluid through the heat exchangers in response to a thermocouple signal. A 10-kW electrical heater powers the exchanger used for the heating cycle, and a 7.5-ton two-stage refrigeration unit is used for the cooling cycle. The chamber temperature can be taken from ambient to either −20 °C or +100 °C in less than 4 h. The ±0.5 °C control of the fluid temperature provided by this system results in regulation of the chamber air temperature to better than ±0.2 °C due to the large heat capacity of the chamber.

The chamber walls are insulated with 1 in. of fiberglass insulation and 2 in. of polyurethane foam and are covered with an aluminum sheath. Further details of this system and its performance specifications are reported elsewhere (*15, 16*).

Prior to each experiment, the chamber was evacuated to at least 10^{-4} Torr. After we filled the chamber with purified matrix air (*23*) at the desired temperature and relative humidity, reactants were added and allowed to mix for at least 30 min. During the course of a run, sampling consumed approximately 2% of the reaction mixture per hour; the chamber pressure was maintained by the addition of purified air (at room temperature) from a Teflon bag outside the chamber. Absolute light intensity within the chamber was determined periodically using NO_2 actinometry (*25*). Relative spectral distributions were obtained with a double monochromator–photomultiplier system located at the far end of the chamber facing the solar simulator through the chamber end windows. Temperature was monitored using thermocouples, pressure with a Validyne gauge, and relative humidity with a Brady array (*16*).

Methods and reliabilities for monitoring reactants and products are described in detail elsewhere (*15, 16, 24*). Ozone, NO, NO_2, and NO_x were monitored by chemiluminescence methods, and CO, organics, and peroxyacetyl nitrate (PAN) and organic nitrates by gas chromatography. Known interferences by PAN and organic nitrates on commercial chemiluminescence NO_x analyzers (*26*) were corrected for by subtracting the chromatographically determined PAN and organic nitrate concentrations from the NO_2 readings.

Reactants and Conditions Employed. Five different reactant mixtures were irradiated at a variety of temperatures. Specific initial concentrations and temperature ranges employed were: (a) propene ~0.5 ppm, NO_x ~0.6 ppm, T = 16–29 °C, (b) propene ~1 ppm, NO_x ~0.5 ppm, T = 10–29 °C, (c) propene ~10 ppm, NO_x ~6 ppm, T = 3–59 °C, (d) toluene ~1 ppm, NO_x ~0.5 ppm, T = 8–53 °C, and (e) "surrogate" mixture ~2.5 ppmC, nonmethane hydrocarbons (consisting of ~40 ppb of ethene, ~80 ppb of ethane, ~40 ppb of acetylene, ~15 ppb of propene, ~17 ppb of *n*-butane, ~12 ppb of *cis*-2-butene, ~110 ppb of 2,3-dimethylbutane, ~10 ppb of 2-methylbutene-2, ~20 ppb of toluene, and ~60 ppb of *m*-xylene), methane ~2.5 ppm, NO_x ~0.25 ppm, T = 5–34 °C. The initial concentrations, temperatures, humidities, and light intensities (as measured by k_1, the NO_2 photolysis rate constant) for these runs are given in Table I.

Results and Discussion

Ozone Formation in "Ambient" Concentration Runs. Table I gives the times of the ozone maxima (if attained), the maximum O_3 concentrations observed, and the O_3 concentrations observed at selected times prior to the maximum for runs at ambient concentrations. Clearly, the rate of ozone formation, as indicated by the times of the O_3 maxima or the 2- or 6-h O_3 concentrations, increases significantly with temperature. Despite this, O_3 formation occurred at the lowest temperatures, and in every case, even at temperatures as low as 5 °C, the ozone concentrations observed after 6 h of irradiation exceeded the federal air quality standard for oxidant at 0.08 ppm.

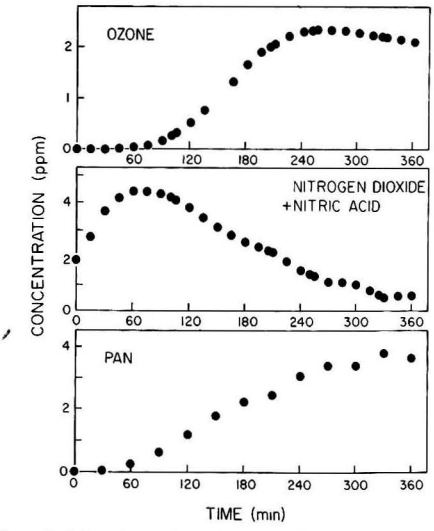

Figure 1. Selected experimental concentration–time profiles for T = 16.1 °C, run no. 193

Thus, while these experiments confirm the previous evidence of a significant and positive temperature effect for photochemical smog formation, they do not support the assertion in the revised air quality criteria document for ozone (*4*) that oxidant concentrations are unlikely to exceed the federal standard at temperatures below ~15 °C. While extrapolation of our smog chamber results to the atmosphere must be done with caution, the observation of high ozone levels (exceeding a first-stage alert in California) on bright and cold ($T \lesssim 11$ °C) days in Denver (*14*) is consistent with our chamber data.

Ozone Formation and NO_x Consumption in Higher Concentration Runs. Table II gives times and levels of the ozone maxima and minima, the times of probable complete NO_2 consumption, and the times of the PAN maxima observed in the high concentration propene runs. In addition, Figures 1–3 show the concentration–time profiles for O_3, NO_2 + HNO_3, and PAN for experiments performed at 16, 33, and 51 °C, respectively. It can be seen that for $T \gtrsim 16$ °C the times of the O_3 and PAN maxima and of estimated NO_x consumption decrease with increasing temperature, while the ozone maximum concentration is relatively unaffected by temperature for $T \gtrsim 11$ °C. On the other hand, the maximum O_3 observed in the 3 °C runs was significantly lower, and occurred earlier than in the higher temperature runs.

In addition to affecting the rates of O_3 formation, temperature was found to affect the shapes of the O_3 concentration–time profiles, particularly with respect to the locations of their maxima relative to the NO_2 and PAN concentration–time profiles. For the T = 15–33 °C runs, the O_3 profile followed the pattern generally observed in ambient concentration runs in that the maximum occurred at or slightly before the time of NO_x consumption and the PAN maximum

Table I. Experimental Conditions and Results of Irradiations of Hydrocarbon-NO_x-Air Mixtures

run	run conditions: av temp, °C	initial concn, ppm: HC	NO	NO_2	light inten[a]	av H_2O, Torr	av RH, %	ozone yields, ppm: 2 h	6 h	max
				Propene Runs						
54	16.0	0.51	0.53	0.06	0.21	7.4	57	0.021	0.130	*b*
52	30.0	0.55	0.52	0.06	0.22	13.7	43	0.020	0.270	*b*
53	38.2	0.55	0.55	0.08	0.21	24.1	48	0.137	0.410	*b*
139	10.3	0.98	0.39	0.13	0.32	3.3	35	0.254		*b*
138	29.5	0.97	0.37	0.14	0.32	2.0	6.5	0.640		0.923
218	2.8	9.89	2.42	2.32	0.42	*d*		0.591		0.591
206	11.1	9.51	3.37	1.88	0.38	~1	14.5	0.892		2.145
193	16.1	9.50	3.96	1.88	0.38	~1	11	0.511		2.340
192	32.8	10.1	4.15	1.88	0.38	~1	5			2.423
211	48.9	10.44	4.51	1.84	0.41	~1	3.5	2.081		*c*
209	50.5	10.64	4.74	1.87	0.39	~1	2.0	2.081		*c*
212	58.9	10.77	4.84	1.95	0.41	~1	1.5	1.96		*c*
				Toluene Runs						
292	7.8	0.94	0.41	0.08	0.39	4.0	49.5	0.034	0.127	*b*
293	29.9	1.07	0.39	0.08	0.39	17	53.0	0.342		0.420
294	52.9	1.11	0.36	0.12	0.39	16.2	15.0	0.491		0.501
				Surrogate Runs						
239	5.0	2.27[f]	0.14	0.10	0.30	~3	~50	0.032	0.086	*b*
240	29.4	2.47	0.15	0.09	0.30	15.7	51	0.117	0.349	*b*
213	33.9	2.57	0.15	0.10	0.40	23.8	60	0.332	0.481	0.481

[a] Light intensity measured by NO_2 photodissociation rate (min^{-1}). [b] Ozone maximum not attained during period of photolysis. [c] See Table II. [d] Tank $O_2 + N_2$ used instead of purified air. Humidity was not monitored, but probably was low. [e] Estimated from propene loss rates, corrected for dilution and reaction of propene with O_3. k(OH + propene) (*35*) and k(O_3 + propene) (*6*) were taken from the literature. [f] First value is estimated from propene loss rates (see footnote *e*). The second

(see Figures 1 and 2). In contrast to this, in the lowest temperature run the O_3 peaked substantially earlier than the time of the PAN maximum and NO_2 consumption (see Figure 2); in the $T \gtrsim 49$ °C runs, the O_3 concentration generally peaked significantly later than the time of NO_2 consumption and the PAN maximum (see Figure 3). Moreover, in the high-temperature runs the O_3 concentrations do not fall following their initial rapid rise; instead they either continue to increase, though at a much slower rate, or, in the case of run 209, decrease slightly and then slowly increase again to produce a double O_3 maximum.

The leveling off of NO_2 readings at a nonzero value after the first ozone maximum is believed to be an artifact due to interference on the NO_2 analyzer (*26, 27*) by HNO_3. HNO_3 unfortunately was not routinely monitored and hence its interference could not be corrected. However, substantial yields of HNO_3 are expected in these runs on the basis of model calculations (*28*), and have indeed been observed by in situ infrared techniques (*29*). It has been assumed in this work that the times at which the NO_2 readings level off correspond to "complete" NO_2 consumption, and that the subsequent "NO_2" measurements are due solely to HNO_3. The increase in these $NO_2 + HNO_3$ readings following the assumed times of NO_2 consumption in the higher temperature runs is attributed to HNO_3 formation from PAN decomposition, as discussed below.

Since O_3 is produced only from the photolysis of NO_2 (*1, 21, 30–34*), the continued formation of O_3 following consumption

Table II. Results for the Irradiation of Propene (10 ppm)-NO_x (6 ppm)-Air Mixtures as a Function of Temperature

	run no. / temp, °C	218 / 2.8	206 / 11.1	193 / 16.1	192 / 32.8	211 / 48.9	209 / 50.5	212 / 58.9
time of NO_2 consumption[a]		~200	~270	~330	~115	~60	~60	~45
PAN max	concn, ppm	0.76	2.90	3.82	3.10	2.42	2.40	2.50
	time, min	210	270	~330	$\gtrsim$115[b]	60	~60	45
"first" O_3 max[c]	concn, ppm	0.59	2.20	2.34	2.42		2.09	
	time, min	120	240	255	110		45	
O_3 local min	concn, ppm						1.99	
	time, min						75	
"second" O_3 max[c]	concn, ppm					2.10	2.08	2.07
	time, min					150	120	90

[a] In the high concentration runs the NO_2 readings on the NO_x analyzer never reached negligible values, probably because of HNO_3 interference (see text). NO_2 was assumed to be consumed when the NO_2 readings stopped declining following the NO_2 maximum. [b] PAN data are highly scattered in this run; the time of the maximum is uncertain. [c] An O_3 maximum that occurs at or before the time of NO_2 consumption is designated the "first" O_3 max, while a maximum which follows the time of NO_x consumption is designated a "second" O_3 max, even if no "first" O_3 maximum preceded it in the run.

estimated quantities, time = t'						expti quantities used in estimations			
time max, h	t', h	HC reacted, ppm	ΔO_3^{corr} $-\Delta NO$, ppm	corr $\Delta O_3 - \Delta NO$/ HC − rct	av [OH], ppht	[HC]$_i$, ppm	integrals, $t = 0 - t'$, ppm/min [O_3]	[O_3][C_3H_6]	[HC]
					e				
>6	6	0.37	0.78	2.1	10.3	0.10	23.9	3.74	87.4
>6	6	0.45	1.04	2.3	10.8	0.05	47.2	5.73	90.6
>6	6	0.50	1.33	2.7	13.7	0.01	93.4	5.66	58.5
>2	2	0.447	0.72	1.6	11.8	0.50	9.18	5.72	90.3
3.75	3.75	0.919	1.79	1.9	21.5	0.02	1.5	18.3	80.1
					f				
2	2	6.21	3.82	0.6	20, 10	3.42	17.2	76.2	772
4	4	9.13	5.57	0.6	21, 15	0.09	228	237	840
4.25	4.25	9.20	8.80	0.96	25, 14	0.06	233	163	789
1.83	1.83	9.81	9.42	0.96	47, 30	0.15	127	150	427
c	0.75	9.59	7.59	0.79	94, 66	0.79	26.0	48.9	251
c	0.75	9.78	9.44	0.97	80, 51	0.77	45.6	110	254
c	0.75	10.35	8.85	0.85	110, 62	0.35	45.8	77.3	211
					g				
>6	6	0.284	0.57	2.0	10.4	0.57	21.4		267
2.75	3	0.426	0.86	2.0	36.1	0.60	39.1		144
2.25	2	0.422	0.90	2.1	59.2	0.65	22.7		106
					h				
>6	6				4.2				
>6	6				18.5				
4.25	4				35.6				

value is estimated from relative *n*-butane/neopentane loss rates. *k*(OH + *n*-butane) (*35*) and *k*(OH + neopentane) (*35*) were taken from the literature. [g] Estimated from toluene loss rates, corrected for dilution. *k*(OH + toluene) (*35*) was taken from the literature. [h] Estimated from 2,3-dimethylbutane loss rates, corrected for dilution. *k*(OH + 2,3-dimethylbutane) (*35*) was taken from the literature. [i] Value given is total nonmethane hydrocarbon in parts per million of carbon.

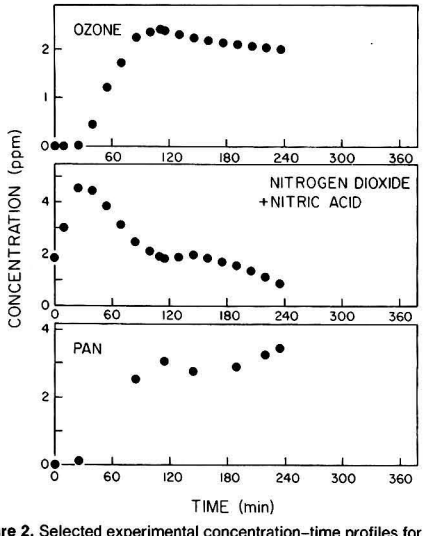

Figure 2. Selected experimental concentration–time profiles for T = 32.8 °C, run no. 192

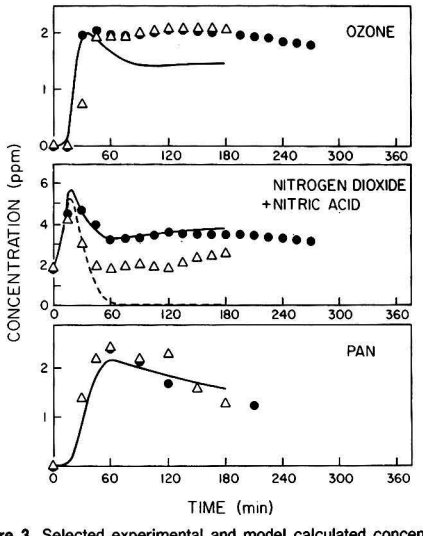

Figure 3. Selected experimental and model calculated concentration–time profiles for T = 48.9 to 50.5 °C runs: run no. 209, (●) experimental; (——) model calculation (O_3, NO_2 + HNO_3, PAN); (- - -) model calculation, NO_2 only; run no. 211, (△) experimental

of the initially present NO_x in the higher temperature, higher concentration runs means that NO_2 must be produced later in the runs by the thermal or photochemical decomposition of nitrogen-containing species formed during the experiment. The major nitrogen-containing species formed in the propene–NO_x–air irradiations include PAN, nitric acid (*27*), and peroxynitric acid (*12, 13*). Of these only PAN is in sufficient concentration and decomposes sufficiently rapidly to provide the postulated source of NO_2. The thermal decomposition of PAN:

$$CH_3COONO_2 \underset{}{\overset{M}{\rightleftharpoons}} CH_3COO\cdot + NO_2 \qquad (1)$$

occurs with a half-life of ~20 min at 27 °C (*10*), and the half-life is known to decrease rapidly with temperature (*10*). Based on the measured activation energy of 26 kcal mol^{-1} (*10*), the rate of the PAN decomposition (reaction 1) is expected to increase by a factor of ~12 for an increase in temperature from ~27 to ~50 °C. Thus, at the higher temperatures encountered in this study, PAN decomposition could provide a source of NO_2 sufficient to permit net ozone formation to continue after the "original" NO_2 has been consumed.

The maximum rates of NO_2 input due to PAN decay can be determined from PAN concentration–time profiles measured during the experiments. As expected, the PAN decay rate following NO_x consumption increased with temperature; it was too low to measure at $T \lesssim 32$ °C, and increased to ~10–15 ppb min^{-1} at T = 49–50 °C, and ~25 ppb min^{-1} at T = 59 °C. The observed rates of O_3 production are, as expected, less than the rates of PAN decay, since other reactions of NO_2, which do not lead to O_3 production, are occurring, and some O_3 is lost at the walls and by reaction with, for example, propene.

Occurrence of a Double Ozone Maximum at High Temperature. The occurrence of the double maximum in the ozone concentration observed in the 51 °C, high concentration propene run 209 can be explained by the changing balance between source and sink processes for ozone. At the time of the first O_3 maximum, reaction with propene is probably the major sink for ozone, with a rate of ~37 ppb min^{-1} (estimated using the observed reactant concentrations and the known propene–ozone rate constant (*6*)). This rate compares with an O_3 wall decay rate of only 0.4 ppb min^{-1} (estimated from the O_3 dark decay constant measured previously in our chamber (*16, 24*)). As the bulk NO_2 becomes consumed, its photolysis does not compensate for the ozone–propene reaction (and other ozone sinks), so that the ozone concentration declines. However, the rate of the ozone–propene reaction decreases as propene is consumed, until it becomes about equal to the rate of PAN decomposition (~10 ppm min^{-1} in run 209), which is by then the major source of NO_2 and thus of ozone. At this time a local minimum in the ozone concentration occurs, after which the PAN decomposition more than balances the ozone sinks. It is clear that these opposing processes are delicately balanced and only under certain conditions will an ozone minimum occur. In fact, such minima were not observed in the otherwise very similar run 211, or in the higher temperature run 212; in these cases a "flat" profile was observed once the ozone maximum was achieved.

The occurrence of the double ozone maxima observed in run 209 was qualitatively simulated by computer model calculations (*21, 28*) employing a detailed mechanism for propene–NO_x–air photooxidations that has been validated (*21*) from propene–NO_x–air and propene–*n*-butane–NO_x–air smog chamber photolyses performed at our laboratories (*16, 24*) under simulated ambient conditions. (The efficiency of radical production from the $O(^3P)$ + olefin reaction was adjusted to fit the initial rates of O_3 and NO_2 formation.) As seen in Figure 3, our model gives good fits to the PAN and the NO_2 + HNO_3 profiles, which tends to validate our assumptions that the interference in the NO_2 readings of the chemiluminescence analyzer is due primarily to HNO_3, and that the leveling off of the NO_2 readings indicates the consumption of initially formed NO_2. (The dashed line in Figure 3 is calculated for NO_2 alone.) The model also gives good fits to the time and level of the first O_3 maximum, and predicts the occurrence of a shallow O_3 minimum at 115–110 min. Although the model predicts that the ozone local minimum occurs somewhat later, and that the O_3 levels at the minimum and the second maximum will be lower than observed experimentally, it can be seen that the observed ozone profile is in qualitative agreement with the current mechanism for smog formation.

Effect of Temperature on Radical Levels. Table I gives the estimated average hydroxyl radical (OH) concentrations for all experiments. They were calculated for the time period 0 to t', where t' (given in Table I) was chosen to be either at or immediately prior to the time of NO_x consumption (or, in experiments where this did not occur, the end of the experiment). The OH radical concentrations were estimated from observed rates of hydrocarbon consumption, since it is generally accepted that hydrocarbons are consumed almost entirely by reaction with OH or O_3 under our conditions (*20, 30–35*). The concentrations were corrected for dilution and (in the case of propene) reaction with O_3. The specific hydrocarbons whose consumption rates were used are given in the footnotes to Table I. Since different hydrocarbons were used to estimate OH levels in different series of runs, the technique is most reliable for obtaining relative changes in OH concentration within a given series of runs rather than for obtaining absolute OH concentrations.

It can be seen from Table I that the average hydroxyl radical concentrations generally increase with temperature for all sets of ambient concentrations runs. For the higher concentration runs, the OH radical concentration appeared to be roughly temperature independent for $T \lesssim 61$ °F and $T \gtrsim 49$ °C. For 16 to 49 °C the OH radical concentration increased with temperature.

The observed dependence of radical levels on temperature could be caused by a number of factors. At the higher temperatures (i.e., $T \geq 49$ °C), the decomposition of PAN, whose formation amounts to a radical recombination sink, leads to net lower radical loss rates. At the lower temperatures, the slower decomposition of HO_2NO_2 allows its formation to become an important radical sink. Moreover, radical initiation processes such as reactions of olefins with O_3 and $O(^3P)$, reactions in the aromatic system forming highly photoreactive ring cleaved intermediates (probably α-dicarbonyls (*36*)), and radical input from "chamber effects" (*19–21*) may be temperature dependent. It is not possible to decide the relative contribution of the various factors leading to enhanced radical concentrations at higher temperatures, since these temperature dependences remain uncertain.

Effect of Temperature on NO to NO_2 Conversion. The formation of O_3 in photochemical smog is attributed to the conversion of NO to NO_2 by the radicals formed by the hydrocarbon consumption reactions. The amount of NO converted to NO_2 can be estimated from the expression: corr ΔO_3 − ΔNO. This is the sum of the amount of NO consumed and the corrected amount of O_3 formed after the NO is consumed. (The observed ozone yields are corrected for amounts consumed by photolysis, reactions with olefins, and heterogeneous decay to obtain an estimate of the total amount formed.) These quantities are given in Table I for the propene and the toluene runs. It can be seen from Table I that while both the estimated amounts of NO to NO_2 conversion and the estimated amounts of hydrocarbon consumed increased significantly with temperature, their ratio is remarkably temperature independent for the ambient concentration runs, and for the high concentration runs where $T > 11$ °C. These results suggest that, at least in the propene and toluene systems with $T > 11$ °C, the temperature does not significantly influence the efficiency of the hydrocarbon consumption reactions in converting NO to NO_2.

Conclusions

Smog chamber irradiations of hydrocarbon–NO_x–air mixtures employing three different hydrocarbon mixtures and a range of reactant concentrations experimentally confirm that temperature has a significant effect on photochemical smog formation over a range of atmospherically relevant temperatures (e.g., 3–52 °C). In general, the rates of all major

manifestations of smog formation, such as ozone formation, hydrocarbon, and NO_x consumption, and NO to NO_2 conversion, increase with increasing temperature. This appears to be primarily due to increasing radical concentrations in smog systems (through increasing rates of radical initiation reactions) or reduced efficiency of radical termination reactions, or both.

On the other hand, temperature appears to have relatively less effect on the ozone formation potential of hydrocarbons, provided sufficient time is allowed for equal amounts of hydrocarbon to react at the lower temperatures as reacted at higher temperatures. Although reduced smog manifestations are observed at low temperatures, our smog chamber results show that it is possible for O_3 levels to exceed the federal air quality standard of 0.08 ppm at approximately 5 °C in hydrocarbon–NO_x systems simulating polluted ambient atmospheres, at least in multiday episodes. Clearly, it would be of interest to have additional ambient air monitoring data taken for the case of low temperatures over a wide range of emission loadings and meteorological conditions from locations at northern latitudes.

In experiments performed at temperatures greater than ~40 °C we have found that ozone concentration–time profiles can be significantly different than those observed at lower temperatures. At lower temperatures, ozone formation generally ceases after the NO_2 is depleted, but at higher temperatures the decomposition of PAN can provide a sufficiently large source of NO_2 to allow continued net ozone production, albeit at a much lower rate than earlier in the experiment. Furthermore, the balance between the destruction of ozone and the ozone-producing reactions can, under appropriate conditions, lead to an ozone concentration–time profile that exhibits more than one maximum. To our knowledge, this has not been observed previously for static smog simulations.

It should be noted that in experiments where the temperature is varied, either the relative humidity or the total water concentration must also vary (except in completely dry systems). The data given in this report are insufficient to determine whether the variation in humidity or water concentration has a significant effect, but preliminary results of other experiments performed in our laboratories suggest that such effects are small compared to those of temperature, at least for the propene and the surrogate systems. Further experiments concerning those effects are planned, and will be described in subsequent reports.

Although our observations concerning the effect of temperature on photochemical smog formation can be qualitatively accounted for in terms of current photochemical models, the predictive capabilities of the models concerning these effects do not appear to be totally satisfactory, and they may very well have errors in important areas relating to temperature effects. Further basic studies of the temperature dependences of the mechanisms and products of ozone–olefin reactions, $O(^3P)$ + olefin reactions, and aromatic photooxidations are required. Furthermore, a much better understanding of temperature and humidity dependences of smog chamber characteristics affecting radical initiation is required before temperature effects observed in smog chambers can be reliably applied to predicting temperature effects in smog formation in the ambient atmosphere.

Note Added in Proof

After this article had been submitted, the federal air quality standard for ozone was revised upward from 0.08 to 0.12 ppm (1-h average) by the EPA administrator.

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Interchange of Metals and Organic Matter between Water and Subbituminous Coal or Lignite under Simulated Coal Slurry Pipeline Conditions

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■ The uptake of metals and organic matter from granular subbituminous coal and lignite by water was investigated under simulated coal slurry pipeline conditions. The metals present at levels well over 1 ppm in both types of coal were Fe, Ca, Mg, Al, Na, K, Mn, Pb, Cu, Zn, Co, Ni, Cr, and Li. Of these, Pb, Co, Ni, and Cr were not detectable by flame atomic absorption in the slurry water separated from the coal. The percentage of metal extracted from the coal varied widely with the type of metal and with the coal/water ratio in the slurry, spanning a range of 0.01 to 75%. Humic acids were present at coal percentages below 5% and were shown to be involved in the solubilization of iron, copper, and aluminum.

The developing need for large-scale transport of abundant resources of Western U.S. coal to Eastern and Southeastern markets has increased interest in coal slurry transport. Basically, this method of transport consists of pumping a mixture of approximately half granular coal and half water through a pipeline. The use of slurry pipelines for the transport of mineral commodities dates back to the 1800's. The first commercial coal slurry pipeline in the U.S. was a 108-mile line operated by the Consolidation Coal Company between Cadiz, Ohio, and Eastlake, Ohio, starting in 1957. This line operated very successfully for 6 years before closing due to increased efficiency of competitive rail transport. At the present time, the only coal slurry pipeline operating in the U.S. is the 273-mile Black Mesa pipeline transporting a coal slurry from the Black Mesa mine in northeastern Arizona to the Mojave Power Project in Southern Utah. In succcessful operation since 1970, this line moves about 5 million tons of coal each year. The successful experience with previous coal slurry lines has provided impetus for proposals for additional lines. Among these are a 1040-mile long line proposed to carry 25 million tons of coal per year from the Powder River Basin near Gillette, Wyo., to a site near White Bluff, Ark., and a very large 1500 mile long pipeline to carry coal from eastern Kentucky to Florida and Georgia.

Typically, coal to be transported by pipeline is ground to below 14 mesh, such that no more than 20% of the solids are below 325 mesh (*1, 2*), stored in tanks under water, and pumped through the pipeline as a 50% slurry in water. At the power plant the slurry is dewatered by centrifugal dryers to about 25% moisture, pulverized with additional removal of surface moisture, and blown into the furnace with heated air. The energy penalty exacted by moisture in the coal requires as much removal of water as possible; the water must be used or disposed of in an environmentally acceptable manner.

Water requirements are a major disadvantage of coal slurry lines, particularly in that most lines are proposed for shipment of coal from arid regions. However, to place the water problem in perspective, it should be noted that generation of electricity at the mine site or conversion of the coal to a liquid or gaseous fuel requires more water than does slurry pipeline transport. For example, genetation of 1 million Btus of electrical energy at the mine site requires 100 gal of water, on-site generation of synthetic natural gas with the same energy content requires 30 gal of water, and only 12 gal of water is required for the slurry transport of coal with an equivalent amount of energy (*3*).

The disposal or use of water at the terminus of a coal slurry pipeline is a major environmental consideration with this technology. Use of the water as makeup water in the power plant's cooling system is a beneficial use, although pollutants in the water have the potential to cause air pollution problems. Discharge of the water into receiving waters requires that it meet pollution standards. These problems may be aggravated if low-grade groundwater is used for slurry transport. Because of pollution problems involving slurry water use or disposal, it is necessary to have as much information as possible about the effects of coal upon the quality of water used for a coal slurry. It should be stressed that these effects can be either harmful or beneficial depending upon whether pollutants are leached from the coal and its associated mineral matter into the water, or if the coal sorbs pollutants from the water. Both types of effects may occur. This paper addresses the question of potential pollutants, especially metal ions, leached from coal into water under simulated slurry pipeline conditions.

Few published studies have addressed the question of coal/water interactions, such as might occur in slurry pipelines. Preliminary results of one such study (*4*) have indicated some coal/water interaction when a 40:60 by weight coal/water slurry was pumped through a closed-loop pipe with a centrifugal pump and when individual flasks containing the same mixture were continuously rocked (both methods gave essentially identical results). Both fresh water from surface water sources and saline water were used in these studies. After 1 day of contact, the concentrations of arsenic, cadmium, chromium, and lead increased slightly, but remained less than 0.050 mg/L, whereas manganese and zinc concentrations increased approximately two and one orders of magnitude, respectively, to reach concentrations of 0.3 mg/L each. The raw water used in the slurry contained a relatively high concentration of copper, which was observed to decrease slightly after

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Table I. Metal Concentrations (Parts per Million) in Subbituminous and Lignite Coal

metal	subbituminous	lignite
Fe	0.50 ± 0.08%	1.4 ± 0.2%
Ca	1.1 ± 0.1%	1.9 ± 0.1%
Mg	0.21 ± 0.04%	0.62 ± 0.08%
Al	1.3 ± 0.1%	0.64 ± 0.06%
Na	0.057 ± 0.006%	0.12 ± 0.05%
K	0.044 ± 0.006%	0.044 ± 0.002%
Mn	53 ± 6 ppm	150 ± 4 ppm
Pb	53 ± 12 ppm	27 ± 4 ppm
Cu	44 ± 2 ppm	17 ± 1 ppm
Zn	49 ± 5	16 ± 2 ppm
Co	12 ± 4 ppm	15 ± 8 ppm
Ni	8.8 ± 5.0 ppm	14 ± 1 ppm
Cr	15 ± 1 ppm	7.6 ± 0.5 ppm
Li	6.2 ± 0.2 ppm	2.6 ± 0.1 ppm
Ag	0.6 ± 0.1 ppm	0.4 ± 0.1 ppm

1 day of contact with the coal. No detectable change in mercury concentration was observed. Alkalinity was found to increase by a factor of four after the first day and continued to increase with time. Sulfates immediately increased from 15.1 to 89 mg/L, then stabilized. Chlorides, nitrates, and pH all increased slightly, but total organic carbon increased from 2.15 to 21.0 ppm. A similar study has been conducted on subbituminous coal from Gillette, Wyo., using distilled water and treated municipal wastewater for the slurry medium, yielding comparable results (*5*). Solutes in the water that were below detectable limits included chromium, copper, manganese, mercury, phosphate, and zinc.

Coal contains a number of components that can contribute pollutants to water used in a coal slurry. Organic substances, particularly humic substances in lower rank coals, can be leached into water from the coal organic matter. Coal contains a variety of mineral matter including primarily clays, alkaline earth carbonates (limestone, dolomite), sulfides (e.g., pyrite, FeS_2), and silica. Of particular significance are the trace elements, including elements from throughout the periodic table. A survey of 101 coals, primarily from the Illinois Basin, has shown (*6*) the presence of the following trace elements substantially above the part per million level: As, B, Be, Br, Cd, Co, Cr, Cu, F, Ga, Ge, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, V, Zn, and Zr. These elements may be associated with either the organic or mineral fraction of coal and potentially may be leached from the solid coal into the slurry water.

This investigation was undertaken to determine solubilization of trace elements and organic matter from carefully characterized samples of subbituminous coal and lignite under simulated coal slurry pipeline conditions. In these studies distilled water was used as the slurry medium so that the maximum effect of the coal upon the water quality could be determined.

Experimental

Trace Element Analysis of Coal. Subbituminous coal from the Powder River Basin of Wyoming and lignite from North Dakota were sampled to obtain representative samples. One-gram portions of the sample were accurately weighed into a crucible and dry-ashed in an oven at 550 °C for 8–12 h. The ash was then transferred to a Teflon cup and 2 mL of aqua regia and 0.2–0.3 mL of HF were added. The Teflon cup was placed inside a metal bomb and heated at 150 °C for 3–4 h to completely digest the ash. The samples were then diluted to 50 mL and analyzed by flame atomic absorption (Perkin-Elmer Model 403) using standard addition. Interference effects were reduced by adding 2000 ppm of lanthanum for calcium and magnesium analysis, 2000 ppm of sodium for potassium and aluminum analysis, and 1000 ppm of potassium for sodium analysis. Each of the coal samples was analyzed in triplicate for calcium, magnesium, lithium, zinc, cadmium, copper, silver, sodium, aluminum, potassium, chromium, iron, nickel, cobalt, lead, and manganese, as shown in Table I.

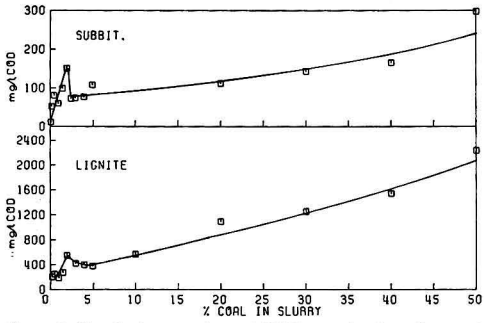

Figure 1. Chemical oxygen demand (COD) as a function of percent coal in subbituminous and lignite slurries

Preparation and Mixing of Slurries. Both coals used in this study were maintained in a closed container in air at 100% relative humidity prior to processing. The coal was reduced in size with a blender operating at low speed. To avoid preleaching the coal, water was not added during grinding, and the speed was kept low to avoid excess pulverization or heating. After grinding, the coal was shaken through 20 and 200 mesh wire screens. Stock coal mixtures were made up to consist of 75% solids between 20 and 200 mesh and 25% solids less than 200 mesh. From 50 to 200 mL of slurry was prepared ranging from 0.1 to 50% coal by weight. The slurries were contained in sealed flasks and stirred by magnetic stirrers for 24 h. Immediately after stirring, the contents of the flasks were transferred to 50-mL centrifuge tubes and centrifuged for 1 h. The water was separated and analyzed for metal content, chemical oxygen demand (*7*), acidity, and pH.

Metal Analysis in Slurry Water. Samples of slurry water not requiring digestion were adjusted to 1% HNO_3 (volume/volume ratio) with concentrated HNO_3 in a volumetric flask and analyzed by flame atomic absorption. Samples containing humic acid were boiled to dryness after 2 successive additions of 2 mL of concentrated HNO_3 and diluted to volume.

Determination of Slurry Water Acidity. Aliquots of 15–100 mL of centrifuged slurry water were titrated potentiometrically with 0.005 N NaOH in a nitrogen atmosphere.

Results and Discussion

In order to understand some of the results obtained with the metals, it is instructive to consider plots of chemical oxygen demand (COD) vs. percent coal in the slurry shown for both subbituminous coal and lignite in Figure 1. Examination of this figure shows that there is a generally increasing COD level with increasing coal/water ratio for both subbituminous coal and lignite; the latter gives higher COD values. Furthermore, both coals show distinct evidence of a peak in COD levels at ca. 2% coal. In this vicinity, the water has a definite yellow color (from the subbituminous slurry) or brown color (from the lignite slurry), and acidification of both solutions yields a characteristic flocculent humic acid precipitate. Acidification of water from the subbituminous coal slurry does not yield a humic acid precipitate at coal/water ratios exceeding approximately 5%. These interesting results can be explained by the solubilization and reabsorption of humic substances at increasing coal/water ratios. Although bitumi-

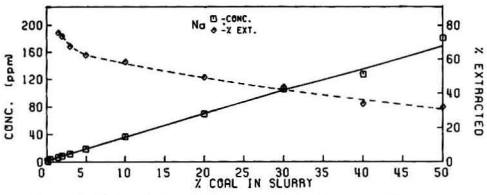

Figure 2. Extraction of Na^+ from subbituminous coal in a slurry

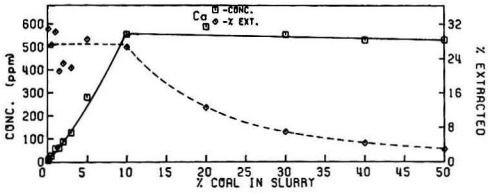

Figure 3. Extraction of Ca^{2+} from lignite in a slurry

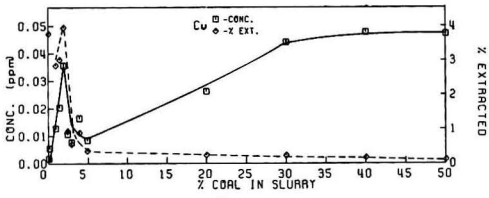

Figure 4. Extraction of Cu^{2+} from subbituminous coal in a slurry

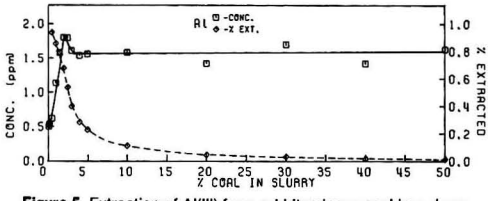

Figure 5. Extraction of Al(III) from subbituminous coal in a slurry

nous coal contains essentially no humic acid inherent to its structure, subbituminous coal is ca. 8.5% humic acid and lignite is ca. 27% humic acid (*8*). At slurry concentrations of only about 2% coal, humic matter leaches from the coal and makes the primary contribution to COD. As the coal/water ratio increases, the humic matter is reabsorbed, and other lower molecular weight organic compounds make up the major contribution to COD.

The metal levels in slurry water were expressed in two ways as a function of increasing percentage of coal in the slurry. The first of these is a plot of metal concentration in the water vs. percent coal in the slurry. To emphasize the effect of coal proportions on metal concentrations in the slurry water, the data were also plotted as percent metal extracted as calculated from the following formula:

$$\%\ \text{metal extracted} = \frac{\text{total mass of metal in slurry water}}{\text{total mass of metal in coal prior to slurrying}} \times 100 \quad (1)$$

Selected plots of these parameters are shown in Figures 2–5.

Plots of metal concentration vs. percent coal show three general types of behavior, as illustrated in Figures 2–4. The first of these is an essentially linear increase of metal concentration with percent coal ash shown for Na^+ ion leached

Table II. pH and Acidity for Lignite and Subbituminous Slurry Water

% coal in slurry	lignite		subbituminous[a]
	pH	acidity, mequiv/L	pH
0.1	4.21	0.108	4.96
0.2	4.05	0.122	4.92
0.5	3.97	0.687	4.92
1.0	3.84	0.568	4.82
1.5	3.83	0.820	4.78
2.0	3.83	1.81	4.76
2.5	3.78	1.34	4.75
3.0	3.76	1.38	4.71
4.0	3.63	1.51	4.65
5.0	3.59	1.53	4.61
10.0	3.57	1.78	4.57
20.0	3.53	3.15	4.58
30.0	3.47	3.21	4.41
40.0	3.49	4.55	4.43
50.0	3.50	5.31	4.34

[a] Acidity values are not given for subbituminous coal because insufficient organic acid was leached from it to enable titration.

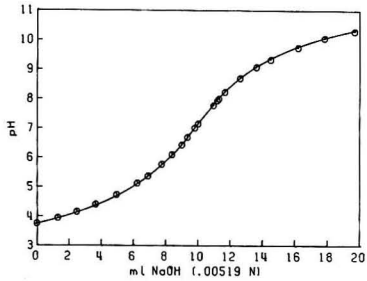

Figure 6. Titration of water from 5% lignite slurry

from subbituminous coal in Figure 2. Such a plot implies an equilibrium of the type:

$$(\text{coal})^-\text{Na}^+ \rightleftarrows (\text{coal})^- + \text{Na(aq)}^+ \quad (2)$$

in which the Na^+ species in water does not exceed any water solubility limit. It may also be due in part to soluble salts, such as NaCl or $NaHCO_3$ in the coal matrix. The second general type of behavior observed is exemplified by Ca^{2+} extraction from lignite as shown in Figure 3. This behavior shows an essentially linear increase in Ca^{2+} concentration up to a point where the Ca^{2+} concentration abruptly levels off and does not increase further with increasing percentage of coal in the slurry. Such behavior would be observed if the solubility product of a calcium salt in water is exceeded. The third general type of behavior observed is shown for the extraction of Cu^{2+} from subbituminous coal in Figure 4. The distinguishing feature of this plot is a peak in the vicinity of 2–3% coal in the slurry. This peak coincides with the maximum humic acid concentration in the slurry water and is readily explained by formation of soluble metal humates in the water. Aluminum from subbituminous coal shows extraction behavior that does not coincide exactly with any of the three preceding general schemes, as illustrated in Figure 5. It is seen that the Al(III) concentration peaks abruptly at 2–3% coal, then remains totally level with increasing coal concentration.

Organic acids leached into the slurry water produce titratable weak acids in the water. In the case of subbituminous

Table III. Metals in Subbituminous Coal Slurry Water as a Function of Percent Coal

metal	metal content of coal, ppm	concn of metal in H_2O, ppm (% metal extracted from coal), for % coal in slurry designated									
		1[a]	1.5	2	3	5	10	20	30	40	50[b]
Li	6.2		0.003	0.003	0.005		0.013	0.012	0.025	0.040	0.070
			(2.98)	(2.53)	(2.41)		(1.90)	(0.75)	(0.94)	(0.96)	(1.14)
Na	570		6.5	8.5	11.8	18.6	36.8	69.8	106.0	127.5	181.2
			(75.4)	(73.3)	(67.2)	(62.1)	(58.2)	(49.1)	(43.5)	(33.7)	(31.9)
K	435		0.56	0.70	0.91	1.40	2.68	4.74	6.55	7.46	8.98
			(8.42)	(7.88)	(6.74)	(6.09)	(5.54)	(4.35)	(3.51)	(3.51)	(2.06)
Mn	53	0.07	0.11	0.15	0.20	0.34	0.63	1.46	2.16	2.40	2.68
		(13.7)	(14.2)	(14.1)	12.1)	(12.1)	(10.8)	(11.1)	(9.6)	(6.8)	(5.1)
Mg	2 110	6.1	9.6	13.3	19.4	29.9		134.2	223.5	266.5	300.0
		(28.4)	(30.0	(31.0)	(29.8)	(26.9)		(25.4)	(24.7)	(18.9)	(14.4)
Ca	11 130	14.7	23.5	34.1	45.4	76.2	145.8	348.8	553.0	551.5	553.0
		(13.1)	(13.9)	(15.0)	(13.2)	(13.0)	(11.8)	(12.5)	(11.6)	(7.43)	(4.97)
Fe	4 980	0.216	0.265	0.310	0.175	0.165	0.249	0.200	0.376	0.295	0.400
		(0.35)	(0.35)	(0.30)	(0.11)	(0.06)	(0.04)	(0.01)	(0.02)	(0.01)	(0.01)
Cu	44	0.013	0.020	0.036	0.008	0.008		0.026	0.044	0.048	0.047
		(2.84)	(3.02)	(3.95)	(0.56)	(0.36)		(0.24)	(0.23)	(0.16)	(0.11)
Zn	49			0.032	0.022	0.038	0.056	0.110	0.148	0.157	0.156
				(3.19)	(1.46)	(1.46)	(1.04)	(0.90)	(0.71)	(0.48)	(0.32)
Al	13 110	1.13	1.58	1.80	1.61	1.56	1.58	1.42	1.70	1.42	1.63
		(0.86)	(0.80)	(0.68)	(0.40)	(0.23)	(0.11)	(0.04)	(0.03)	(0.02)	(0.01)

[a] Designates a slurry of 1% coal in water. [b] Designates a slurry of 50% coal in water.

Table IV. Metals in Lignite Slurry Water as a Function of Percent Coal

metal	metal content of coal, ppm	concn of metal in H_2O, ppm (% metal extracted from coal), for % coal in slurry designated									
		1[a]	1.5	2	3	5	10	20	30	40	50[b]
Li	2.6	0.008	0.008	0.011	0.017	0.029	0.050	0.111	0.174	0.252	0.340
		(32.4)	(20.3)	(20.5)	(21.2)	(21.6)	(17.5)	(17.5)	(15.9)	(14.8)	(13.3)
Na	1 200	8.4	11.6	17.8	27.0	39.8	82.2	151.5	204.0	260.0	315.8
		(69.1)	(63.2)	(72.5)	(72.6)	(62.9)	(61.5)	(50.2)	(39.5)	(32.4)	(26.3)
K	440		0.57	0.83	1.20	1.81	3.60	5.55	6,41	7.06	8.08
			(8.36)	(9.13)	(8.67)	(7.70)	(7.25)	(4.98)	(3.35)	(2.37)	(1.81)
Mn	147	0.37	0.40	0.71	1.10	2.02	4.06	6.05	6.90	7.72	8.70
		(24.8)	(18.0)	(23.7)	(24.1)	(26.1)	(24.8)	(16.4)	(10.9)	(7.9)	(5.9)
Mg	6 240	25.0	35.2	51.9	76.1	137.8	280.0	474.2	600.0	739.1	856.2
		(39.6)	(37.0)	(40.8)	(39.4)	(41.9)	(40.4)	(30.2)	(22.4)	(17.8)	(13.7)
Ca	18 740	57.0	59.9	87.2	126.3	280.1	554.5	587.0	553.0	529.5	531.0
		(30.1)	(21.0)	(22.8)	(21.8)	(28.4)	(26.6)	(12.5)	(6.9)	(4.2)	(2.8)
Fe	14 440	1.04	1.79	3.79	1.89	1.08	0.83	1.12	1.44	1.48	2.35
		(0.72)	(0.82)	(1.29)	(0.42)	(0.14)	(0.05)	(0.03)	(0.02)	(0.02)	(0.02)
Cu	17.3	0.024		0.041	0.015	0.016		0.050	0.076	0.054	0.057
		(13.9)		(11.6)	(2.7)	(1.8)		(1.2)	(1.0)	(0.5)	(0.3)
Zn	16.5		0.051	0.062		0.062	0.167	0.175	0.186	0.181	0.207
			(20.3)	(18.5)		(7.1)	(9.1)	(4.2)	(2.6)	(1.6)	(1.2)
Al	6 420	0.92	1.45	2.69	2.31	2.43	4.48	6.58	6.55	7.29	8.62
		(1.43)	(1.48)	(2.06)	(0.99)	(0.72)	(0.63)	(0.41)	(0.24)	(0.17)	(0.13)

[a] Designates a slurry of 1% coal in water. [b] Designates a slurry of 50% coal in water.

coal the organic acid content was too low to give meaningful titrations. However, good titration curves were obtained with water from lignite slurries as shown in Figure 6. The acidities of lignite slurries and the pH values of lignite and subbituminous coal slurries are expressed in Table II.

Space does not permit showing plots of metal concentration and percent metal extracted vs. percent coal in the slurry for all the metals studied in both subbituminous coal and lignite. These plots are given in a thesis on the subject (*9*). However, Table III summarizes the data obtained from subbituminous coal and Table IV summarizes the metal extraction data for lignite. In the case of subbituminous slurries, the metals showing "type 1" behavior, in which there is a regularly increasing concentration of metal in slurry water with increasing percentage of coal in the slurry, include lithium, sodium, and potassium. Metals in subbituminous coal slurries showing "type 2" behavior with a distinct plateau are manganese, magnesium, calcium, and zinc. Metals in subbituminous coal slurries showing "type 3" behavior with a peak coinciding with peak humic acid concentration are iron, copper, and alumi-

num. In lignite slurries the "type 1" metals are lithium, sodium, and magnesium; the "type 2" metals are potassium, manganese, calcium, and zinc; and the "type 3" metals are iron, copper, and aluminum. It is significant to note that the percentage of metal extracted from the coal decreases with increasing coal/water ratio for all metals, and that in many cases only a very small percentage of the total metal in the coal is extracted in a slurry containing around 50% coal. Both of these factors are very favorable insofar as the quality of coal slurry wastewater is concerned.

Lead, cobalt, and chromium were not detectable in the slurry waters by flame atomic absorption. Although these metals were present in the subbituminous coal and lignite at appreciable levels, their absence in the coal slurry water is quite favorable from the environmental viewpoint.

Zinc, iron, and copper are known to be present as low-solubility sulfides in coal, although their solubilities could be increased in the acidic slurry or by oxidation of sulfide to sulfate. Aluminum is found in several insoluble inorganic forms in coal, which should limit the solubility of aluminum in slurry water. The solubilities of these metals are higher than would be predicted from the solubilities of their inorganic forms, indicating that organic chelates formed with coal organic matter may be present in the slurry water.

Aluminum hydroxide precipitates at pH values above 4 and is probably a limiting factor in the concentration of aluminum observed in subbituminous coal slurries. The lignite slurry waters have pH values lower than the subbituminous coal slurry waters, probably explaining why the aluminum concentration in the subbituminous slurry is lower than that in the lignite slurry, even though the subbituminous coal contains twice as much aluminum as the lignite. The solubility of inorganic iron(III) does not appear to limit the concentrations of iron in the slurry waters. The soluble iron is probably present as organically bound iron or as soluble iron(II).

There is very little difference in pH between 1 and 50% slurries of both lignite and subbituminous coal. Therefore, the data are probably insufficient to discern any influence of pH upon metal extraction from coal. In most practical applications of the coal slurry pipeline, it is likely that the pH of the slurry water will be determined and buffered by the mineral matter in coal and acidic ion exchange groups on the coal surface. However, it is expected that in general more metals would be extracted at lower pH values. In cases where metal leaching from coal might be a problem, it is suggested that lime could be added to keep the pH high enough to reduce leaching while preventing the formation of soluble metal humate complexes through the production of insoluble calcium humate salts.

The inorganic constituents of coal containing sodium, lithium, potassium, and magnesium are soluble to the extent that they would not limit the concentrations of these elements in slurry water. These metals are probably exchanged by cation exchanging groups on the coal surface.

In general, the results of this research present a favorable picture of coal slurry pipeline byproduct water insofar as heavy metals are concerned. The essential absence of lead, cobalt, nickel, and chromium in the water, despite their presence at levels of several parts per million in the coal, is evidence of a low tendency for water to leach these environmentally important heavy metals from coal under coal slurry conditions. The percentages of other metals leached from coal in a 50% slurry are extremely low, e.g., 0.01% for iron, aluminum, and copper in subbituminous coal. Coal even has the ability to retain most of its sodium, which should be highly soluble in the inorganic form (except for that held by ion exchange in clay). Organic levels in the slurry water could cause some water quality problems, although it is anticipated that standard lime treatment would remove a large amount of humic organic material. In summary, these studies have not shown any major coal slurry byproduct water quality problems.

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Mathematical Modeling of Changes in the Distribution of Sulfur in Coal as It Undergoes Mining and Transport Operations

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The time-averaged distribution of sulfur dioxide (SO_2) emissions from a coal-fired electrical generating station completely determines whether compliance with both Federal and State New Source Performance Standards (NSPS) for SO_2 emissions will be achieved. In addition, this distribution, together with atmospheric conditions, determines whether federal and state ambient SO_2 air quality standards will be met in the vicinity of such a station. In light of the increasing importance that coal is expected to play in the national energy picture, the air quality impacts of using coal as fuel for generating stations deserve in-depth consideration.

The distribution of SO_2 emissions is influenced by:

- the composition of the coal that is mined
- the coal handling and processing methods used at the mine, during coal shipment, and at the generating station
- the fuel combustion processes

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■ A model that simulates the effects of mixing on the distribution of the sulfur content of virgin coal as it is mined and transported from the Kayenta Mine to the Navajo Generating Station in Page, Ariz. is described. By knowing the heating value of the coal and assuming that all of the sulfur appears in the form of SO_2 in the product stream, one can translate the sulfur distribution directly into an SO_2 distribution. The basis of this model is the characterization of the coal flow as a continuous stream of discrete parcels of coal, each of known mass and known sulfur content. Mixing in the process is assumed to occur through independent diffusive and block shuffling effects. Transfer functions are developed for each of the intervening unit operations and combined mathematically to reconstruct the entire process. Results indicate that this approach can be used successfully to predict the distribution of sulfur emissions from the plant for both 3- and 24-h averaging times. Although specifically developed for the Navajo Generating Station, the underlying principles in this formulation can be applied to similar situations.

- the air quality control equipment used
- the averaging times for the SO_2 emissions used in the distribution.

During the processing of coal between mining and its use as a fuel, mixing occurs that reduces the variance in the sulfur distribution of the coal at the mine. The mathematical model described here predicts this mixing by modeling the flow of coal throughout processing as a continuous stream of discrete amounts of material of known weight and uniform sulfur content. When fully validated, the model is capable of predicting the distribution of sulfur emissions at the plant stack when supplied only with information characterizing the distribution of sulfur in the source field.

The model described was developed for application to the Navajo Generating Station (NGS) in Page, Ariz., but we believe that its underlying principles are valid more generally. Although our development did not treat the case where control devices were installed, the model can be easily extended for this application if it is assumed that the net effect of the controls is the proportional reduction of the emissions by a constant factor.

The Navajo Generating Station

The NGS is located in northern Arizona on Lake Powell. At full capacity, it produces 2400 MW of electricity from three 800-MW units while consuming approximately 22 000 tons of coal per day. As a byproduct, 220 tons of SO_2 per day is also produced from coal containing 0.5% sulfur.

Coal is supplied to the Navajo site from the Kayenta mine, which lies 90 miles west of the plant in Black Mesa, Ariz. A brief description of the mining and transport operations as the coal moves from mine mouth to boiler, illustrated in Figure 1, is given: (1) At the mine site, approximately 160 truckloads of coal, each holding 180 tons, are mined during the daylight and evening shifts. (2) Once mined, the coal is hauled to a hammer mill, where it is reduced to particles no larger than 2 in. in cross section. (3) After this reduction, one-third of the coal is discharged onto a night storage pile, to be reclaimed during nighttime operations. The remaining two-thirds are shipped overland on a 7.3-mile conveyor belt to the train loading silos. (4) From the conveyor belt, the coal is transferred to four 6000-ton storage silos by means of a carrousel feed mechanism, which fills them sequentially. (5) When a train is filled, the cars are pulled under the silos, and either silos 1 and 2 or silos 3 and 4 are unloaded simultaneously, filling two cars at a time. The process continues until an entire 50-car train, with each car carrying approximately 120 tons, is full. (6) After the 90-mile overland train ride, the coal is unloaded at the NGS. Initially, six cars are pulled over the train unloading hopper and emptied. Then, with the train moving at 4 miles per hour, subsequent blocks of four cars are dumped automatically until the train is entirely emptied. (7) From the train unloading hopper, the coal falls onto a conveyor belt and passes over a magnetic separator. Coal samples are periodically withdrawn from the conveyor belt for further analysis before the coal is divided into the supply for operational use and that for on-site storage for weekend operations. Approximately one-quarter, or 300 tons per hour, of the coal is fed to the on-site storage pile. The remaining three-quarters, or 900 tons per hour, is used in daily operations. (8) The daily supply of coal is divided among the three boilers at the plant surge bin. Then the coal is fed via an overflow mechanism to seven feed silos, each holding 540 tons, assigned to each boiler. (9) As the coal filters through each feed silo, it is ground in a bowl mill until it is less than 60 mesh in size. The streams of coal from the seven bowl mills are combined and fed into the boiler.

During weekend operations, the plant is fed directly from the on-site storage pile. Material is reclaimed, fed to the plant surge bin, and subsequently processed through the remaining transport steps. At night, a similar procedure is used, except that coal is withdrawn from the night storage pile and subsequently processed.

The Mathematical Model

Throughout the mining and transport operations, considerable mixing of the coal occurs. In addition to the mixing between adjacent truckloads, various amounts of coal are interchanged as they are fed to silos, train cars, and receiving hoppers. In our analysis, the flow of coal throughout the transport process was characterized as a stream of discrete lots (N_i) of variable size and sulfur content. At the outset, they were chosen to be equivalent in size to one truckload of coal originating at the mine. However, during the various stages of processing, both their size and sulfur content were allowed

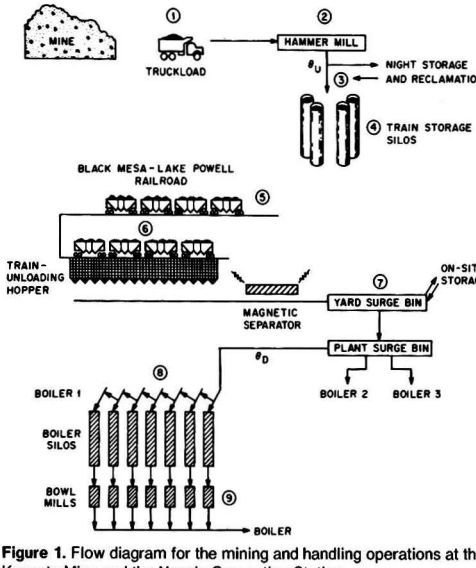

Figure 1. Flow diagram for the mining and handling operations at the Kayenta Mine and the Navajo Generating Station

to vary in accordance with the amount of mixing occurring in a particular operation.

In our model, mixing is divided into two different types that are treated independently: diffusional and block shuffling. The former occurs when adjacent loads of coal interact and homogenize the sulfur content in each sample. The latter results whenever the sequence in which the lots of coal in a particular queue are changed in a predetermined pattern during processing.

For further simplification, we subdivided the process into several individual unit operations, each of which was modeled independently. Among those steps for which transfer functions were developed are: (1) daily mining operations, (2) hammer-mill operation, (3) on-site mine storage and nighttime reclamation, (4) silo loading and unloading, (5) train unloading at the NGS, (6) on-site plant storage and weekend reclamation, and (7) boiler silo storage and bowl mill operation.

As a means of developing the required models, we followed the progress of an individual block of material as it passed through a particular stage of an operation. With knowledge of the sequence of the inlet queue and either the storage or outlet feed arrangement, an algorithm relating the inlet and outlet streams was developed. Aside from the hammer-mill operation, which involves diffusional mixing, this procedure was used in the analysis of each of the above steps.

Diffusional Mixing Model. Although mixing is one of the most common industrial processes, it is poorly understood. Quantification of such processes has been largely empirical, but some theoretical inroads have been made (*1, 2*). In our study, we modeled diffusive mixing using a diffusional shear analysis (*3, 4*) originally proposed by Lacey (*5*) and later developed by Hogg et al. (*6*).

As a means of simulating the intermingling between adjacent blocks of material, the situation was visualized as shown in Figure 2. Material from sample L in the region $-L/2 \leq x \leq 0$ mixes with the material in sample R in the region $0 \leq x \leq L/2$ and vice versa. We have represented the process using a simple Fickian model:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

where c = concentration of sulfur in the region $-L/2 \leq x \leq L/2$, D = diffusion coefficient, x = distance, and t = time.

The boundary conditions are:

$$\frac{\partial c}{\partial x}(t, -L/2) = 0$$

$$\frac{\partial c}{\partial x}(t, L/2) = 0$$

$$c(0, x) = \begin{cases} [\mathrm{Co^L}] \text{ if } -L/2 \leq x \leq 0 \\ [\mathrm{Co^R}] \text{ if } 0 \leq x \leq L/2 \end{cases}$$

Using Laplace transform techniques, we can obtain the solution for the sulfur concentration as given by the following Fourier series:

$$c(x, t) = \frac{[\mathrm{Co^L}] + [\mathrm{Co^R}]}{2} - \frac{2([\mathrm{Co^L}] - [\mathrm{Co^R}])}{\pi} \times \sum_{\eta=1}^{\infty} \left\{ \frac{1}{(2\eta - 1)} \sin\left[\frac{(2\eta - 1)\pi x}{L}\right] \times \exp\left[\frac{-(2\eta - 1)^2\pi^2}{L^2} Dt\right] \right\} \qquad -L/2 \leq x \leq L/2$$

To remove the spatial dependence of this formulation, we can subdivide the original sample lots into half-sizes and consider a new mean value for those areas in the regions $-L/2 \leq x \leq 0$ and $0 \leq x \leq L/2$ given by the integral formulas:

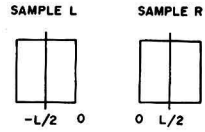

Figure 2. Diagram of adjacent blocks of material

$$\bar{C}_L(t) = \frac{\int_{-L/2}^{0} c(x, t)dx}{-L/2} \qquad -L/2 \leq x \leq 0$$

and

$$\bar{C}_R(t) = \frac{\int_{0}^{L/2} c(x, t)\,dx}{L/2} \qquad 0 \leq x \leq L/2$$

Performing the integrations, we obtain:

$$\bar{C}_L(t) = \frac{[\mathrm{Co^L}] + [\mathrm{Co^R}]}{2} + \frac{4([\mathrm{Co^L}] - [\mathrm{Co^R}])}{\pi^2} \times \sum_{\eta=1}^{\infty} \frac{1}{(2\eta - 1)^2} \exp\left[\frac{-(2\eta - 1)^2\pi^2 Dt}{L^2}\right]$$

and

$$\bar{C}_R(t) = \frac{[\mathrm{Co^L}] + [\mathrm{Co^R}]}{2} - \frac{4([\mathrm{Co^L}] - [\mathrm{Co^R}])}{\pi^2} \times \sum_{\eta=1}^{\infty} \frac{1}{(2\eta - 1)^2} \exp\left[\frac{-(2\eta - 1)^2\pi^2 Dt}{L^2}\right]$$

Since the quantity $Dt/L^2 = \theta$ appears as a lumped parameter for which D, t, and L need not be known individually, the modeling of diffusive processes can be limited to an estimation of a single parameter, θ.

Population Models. In general, the distribution of sulfur in a coal field is not spatially uniform. Its variation is not even monotonic; it can deviate significantly over reasonably short distances. Thus, without a point-to-point analysis, it is impossible to determine the spatial dependence of sulfur in a given field. To circumvent this problem, we have adopted a statistical approach using a distributional model that related the sulfur content of a particular sample to its frequency of occurrence in a given field. Establishing this distribution requires an extensive sampling program, which normally entails drilling a statistically significant number of core samples, analyzing the composition of each core, and then developing a population model.

In our study, we used a γ distribution (*7*) rather than the customary normal curve to represent the in situ sulfur content in the Kayenta field. This distribution has been shown to describe accurately the distribution of sulfur from the Kayenta mine (*8*). Mathematically, the γ distribution is given by:

$$f(x) = \frac{\beta^\alpha}{\Gamma(\alpha)} e^{-\beta x} x^{\alpha - 1} \qquad 0 < x < \infty, \alpha > 0$$

where the parameters α and β are given by the equations:

$$\alpha = \bar{x}^2/s^2$$

$$\beta = \bar{x}/s^2$$

and $\bar{x}$ is the mean of the distribution and s^2 is its variance. Both $\bar{x}$ and s^2 can generally be determined empirically and in our application were obtained from the available core data.

A γ distribution was also used to characterize the distribution of sulfur at both the mine site and the yard site storage

locations. In these cases, the parameters α and β were computed using the elementary formulas:

$$\bar{x} = \frac{\sum_{i=1}^{N_j} x_i}{N_j}$$

$$s^2 = \sqrt{\sum_{i=1}^{N_j} \frac{(x_i - \bar{x})}{N_j - 1}}$$

where x_j is the homogeneous sulfur content of an individual block of material deposited on a coal pile j, which was originally obtained from the mine field, and N_j are the number of blocks used to constitute that pile.

Sampling Techniques. During daily operation, coal is continuously withdrawn from the mine and is stored at the mine or the plant. Later, at night or on the weekend, this material is reclaimed and used. To model these mining activities, we assumed that whenever coal was withdrawn from a site, discrete amounts were taken, each of which had a homogeneous sulfur content. This assumption appeared to be justified because this quantity of coal is very small compared with the quantity burned over any significant combustion time (or averaging time). With this proviso, random sampling techniques were then used to simulate the sampling process.

Mathematically, this technique entailed first generating a random number from a uniformly distributed population in the open interval $0 < \Phi < 1$. Then, from a standard normal curve:

$$\Phi = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{Z_\Phi} e^{-Z^2} dz$$

we determined the normal variable Z_Φ corresponding to the random cumulative index Φ. The value Z_Φ was subsequently substituted into the Wilson–Hilferty transformation:

$$\chi_\Phi = \frac{\alpha}{\beta}\left(1 - \frac{1}{9\alpha} + Z_\Phi \sqrt{\frac{1}{9\alpha}}\right)^3$$

to compute the random γ variable χ_Φ corresponding to the sulfur content of a particular sample. The variables α and β have the same definitions given earlier.

Experience has shown that this approximation is most accurate in the central part of the distribution and is less accurate in the extreme parts of the tails. We computed the amount of error incurred by this approximation using the method developed by McGinnis and Sammons (*9*). Table I gives the error for two values of the parameter α.

Parameter Estimation. A complete mathematical description of the Kayenta mining and transport operations would require acquisition of a voluminous amount of information, such as empirical data on the distribution of the sulfur content in the inlet and outlet streams of each unit operation previously identified. In addition, data on the composition of streams fed to and reclaimed from storage would have to be obtained. Although this information would be both expensive and time consuming to gather, it would permit the modeling of individual process steps, taking into account both diffusive and block mixing effects.

Unfortunately, most of this information was unavailable for the case we studied, and would not be available in most applications. The available data included: (a) the distribution of sulfur in selected coal fields; (b) the distribution of the daily average dry sulfur content of the coal received at the plant for a base-case field; (c) the distribution of hourly average SO_2 emissions emanating from an operational stack for the same base-case field.

In light of such limited information, we analyzed the process to minimize the number of parameters to be estimated. We identified three values that need be specified for a simulation: (a) A mining range, α_D, representing the limits of the sulfur content of the coal over which daily mining operations can occur. (b) A dimensionless parameter, θ_D, characterizing the downstream diffusive mixing that occurs between the train unloading hopper and the boiler. (c) A dimensionless parameter, θ_U, characterizing the upstream diffusive mixing that occurs between the mine site and the train unloading hopper.

In spite of these further simplifications, only two sets of data were available for estimation of the above three values: the daily dry sulfur averages at the plant site (α_D) and the hourly SO_2 emissions recorded at the stack (θ_D). Through analysis of operational practices at the NGS, we assessed the impact of the third parameter (θ_U).

Experience has shown that, if the entire mine population is sampled on a given day, then the variance in the computed daily average dry sulfur content is less than the observed variance. This finding indicates that only a discrete subset of the entire coal population is mined at any given time. To simulate this phenomenon mathematically, we restricted daily mining activity to a limited segment of the entire coal population, which is characterized by a typical daily value, χ_D, randomly drawn from the entire population and a variation α_D in either direction (±). The situation is shown graphically in Figure 3. Using this approach and base-case data for a field having a mean sulfur content of 0.53 and a standard deviation of 0.17, we parametrically determined that $\alpha_D = 0.45$. Thus, a significant fraction of the mine field sulfur distribution is apparently sampled during a mining day.

Table I. Errors in Approximating a γ Distribution Using the Wilson–Hilferty Transformation for Various Percentiles and α Parameters[a]

α	percentile	error (overestimation), %
$\alpha > 16$	0.1	0.2
	0.0001	0.6
	0.99	0.5
	0.9999	0.1
$\alpha > 4$	0.0001	1.5
	0.01	1
	0.9999	1.2
	0.99	1

[a] In most of the cases treated in this study, $\alpha > 4$.

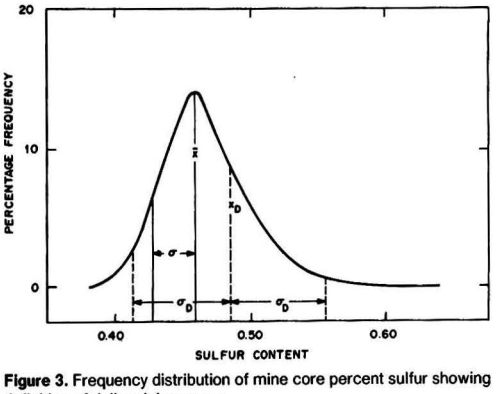

Figure 3. Frequency distribution of mine core percent sulfur showing definition of daily mining range

To establish the downstream mixing parameter θ_D, we used the SO_2 emissions data to calculate sulfur emission rates based on hourly data for coal flow rates and volumetric gas throughputs. We normalized the sulfur distribution by dividing each value by its daily average and then constructing a distribution of these ratios. This procedure reduces the uncertainties associated with determining SO_2 emissions over short averaging times (<24 h) in the effluent stream. Then, in a series of parametric studies, we compared the computed results with observational data. Figure 4 represents our final results, which indicate that $\theta_D = 1.04$.

Having exhausted the available information, we could not rigorously estimate the upstream mixing parameter, θ_U. Fortunately, the conditions at the NGS render absolute determination of this parameter noncritical. At the train unloading hopper at the NGS, four carloads of coal are simultaneously unloaded. Through a simple calculation based on the speed of the conveyor belt, its width, the coal discharge rate, and coal density, it is easy to show that the four carloads are homogeneously blended. Thus, the mixing at this location more than overshadows the diffusive mixing occurring in all the previous processes. A sensitivity analysis, in which a series of parametric runs was made varying the value of θ_U, indicated that the effects of large changes in this parameter on the final 3-h computed average SO_2 concentration were marginal. For completeness, we used a nominal value of $\theta_U = 0.05$ in our simulations.

Model Output. The previously described model with its parameters α_D, θ_U, and θ_D can produce the following distributions for coal from any portion of a mine, given the mean and variance of the input distribution: (a) the daily dry sulfur averages; (b) 3-h averages of the sulfur content of the burned coal for daily operations; (c) 3-h averages of the sulfur content of the burned coal for weekend operations. In addition, the program has been developed with sufficient flexibility to be able to treat cases in which incoming high-sulfur coal from the mine may be mixed with on-site low-sulfur coal at the plant. Such mixing might be necessary when disruptions in the normal low-sulfur coal supply occur.

To extend the validity of the model for a variety of cases beyond the parameter estimation case (referred to as the base case), we had to make certain assumptions about the parameters θ_D and α_D. We assumed that the value of θ_D will not vary as long as the mining and transport operations remain unchanged. For the parameter α_D, we postulated the relationship:

$$\frac{\alpha_D}{\sqrt{s^2}} = \frac{\alpha_D^B}{\sqrt{s_B^2}}$$

where α_D = the daily mining range of any arbitrary coal field, α_D^B = the daily range of the base case (0.45), s^2 = the variance of any arbitrary coal field, and s_B^2 = the variance of the base case (0.029). Our motivation for making this approximation was to allow compensation for either the skewness or the flatness that may occur in sulfur distribution of other mine fields.

Assumptions and Limitations. In developing our model, we made four basic assumptions, discussed below:

• *Representation of Mixing by a Fickian Model.* Since little information is available on mathematical modeling of mixing, this application of the Fickian model represents a practical approach to analyzing the processes involved. Basically, the assumption implied is that alternate layers of material are thinly overlaid in a way that allows mixing. Although some material may be convectively transferred in bulk, as in other transport processes, little information of value is available for evaluating the magnitude of the effect of this process. Using the Fickian model, one need vary only one parameter, θ, to simulate various degrees of mixing, whereas

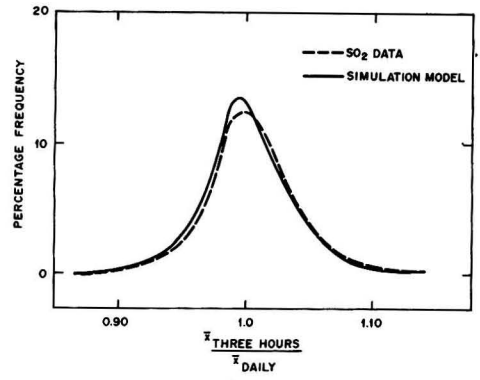

Figure 4. Comparison of observed and predicted distributions of sulfur emissions from the Navajo Generating Station

if convective effects were included, two parameters, V and θ, would have to be specified.

• *Lumped Parameter Representation.* We assumed throughout this analysis that the diffusive mixing process can be separated from any other mixing that might occur in the actual operations. Furthermore, we assumed that the entire bulk of this mixing can be lumped into two categories: pre-train-loading hopper and post-train-loading hopper. In reality, mixing occurs at each step where material is transferred or the contents of a container or conveyor are agitated. To develop an adequate, comprehensive model of the process, we would have to measure the composition of incoming and outgoing streams as they enter and exit each phase of coal handling. This procedure would enable the modeling and parameterization of each piece of equipment independently. Although possible, such a procedure would be very costly, and it may be necessary only if the mining and handling sequence is sensitive to diffusion processes and if those processes were expected to change over the life of the modeled facility.

• *Variance Ratio.* We postulated the relationship:

$$\frac{\alpha_D}{\sqrt{s^2}} = \frac{\alpha_D^B}{\sqrt{s_B^2}}$$

to account for variances in the limits of daily mining activity (α_D) that may occur as arbitrary coal fields are selected (s^2). Using the base values of 0.45 and 0.029 for α_D^B and S_B^2, respectively, indicates that α_D will have a value of approximately $2.64s$, or more than three times the standard deviation of the selected coal field. Although it would be desirable to have data from various coal fields available to confirm this relationship, the value of $+2.64s$ can be interpreted as ensuring that almost the entire population would be sampled on any given day. Hence, it appears that major discrepancies arising from this assumption would be minimal.

• *Uniform Mixing at the Train Unloading Hopper.* At the NGS, 1200 tons of coal per hour is ejected from the train unloading hopper onto a high-speed conveyor belt, which is 4.5 ft wide and which moves at 600 ft/min. Since coal has a density of 50 lb/ft^3, the thickness of the coal layer on the conveyor belt is about 4 in. The hopper unloads through 12 outlet chutes; thus, the contents of any four train cars that are simultaneously unloaded are thoroughly mixed.

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Poisoning of Platinum–Rhodium Automotive Three-Way Catalysts by Lead and Phosphorus

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■ The activity and durability of platinum–rhodium (Pt–Rh) automotive three-way catalysts were investigated as a function of lead (Pb) and phosphorus (P) fuel levels, thermal aging, and catalyst composition. The Pt–Rh catalysts were durability tested in pulse-flame reactors followed by flow reactor steady-state activity measurements. The nitric oxide (NO) and hydrocarbon conversions of low Rh-content three-way catalysts were highly sensitive to even trace levels of Pb in current simulated certification fuel (6 mg of Pb/gal) when compared to contaminant-free fuel. Catalysts having higher Rh content with similar noble metal loadings improved the net NO and hydrocarbon conversions. Increasing the peak temperature in the aging cycle from 730 to 820 °C improved the NO and hydrocarbon conversions because of lower Pb retention. The Pt–Rh three-way catalysts were not poisoned by P.

The successful utilization of noble-metal automotive catalysts necessitates the removal of potential catalytic poisons from the exhaust system. In order to comply with the more stringent emission standards of the future, platinum–rhodium (Pt–Rh) three-way catalysts (TWC) have been developed for the simultaneous removal of nitrogen oxides (NO_x), carbon monoxide (CO), and hydrocarbons (HC) from the exhaust of light-duty motor vehicles. These noble-metal TWCs are susceptible to poisoning by lead (Pb) at the relatively low contaminant levels present in "unleaded" fuels. Rhodium, an active metal component in TWC formulations, is particularly sensitive to poisoning by Pb (*1*). The problem in the widespread use of precious metals in catalytic converters is further intensified because of the shortage of Rh, whose supply is limited to the mine ratio (Pt/Rh = 17/1), i.e., 6% of the amount of Pt found in the precious metal ores (*2*).

Of the three major fuel contaminants [Pb, phosphorus (P), and sulfur (S)], Pb and P are fuel additives, whereas S is present in gasoline in varying amounts depending, in part, upon the origin of the crude oil. Since the introduction of catalytic converters and the availability of unleaded gasoline, Pb and P contamination have continuously declined, while the S content has not changed. Field audit data indicate current contaminant levels of 5 mg of Pb/gal, 0.1 mg of P/gal, and 0.022 wt % S in "unleaded" gasoline marketed across the nation (*3*).

Poisoning of automotive catalysts has been recently reviewed by Shelef et al. (*4*) for both noble- and base-metal catalysts. Poisoning studies of monolithic noble-metal *oxidation* catalysts indicated that at lead levels of ≤70 mg of Pb/gal there exists a correlation between catalytic deactivation rate (especially for hydrocarbon conversion) and the amount of Pb passed through the catalyst (*5,6*). Fuel P was shown to exert a strong poisoning effect on the oxidation catalysts (*7*). Poisoning by Pb and S is considered the most important factor in the deactivation of NO *reduction* catalysts, such as copper–nickel and platinum–nickel catalysts (*8*). Also, the NO reduction activity of ruthenium-containing catalysts was depressed by the presence of fuel Pb and S with only slight poisoning due to P, even though the catalyst retention for P was higher than for Pb or S (*9*). Laboratory evaluations of TWCs (*1,10*) indicated a significant improvement in catalyst durability upon a decrease in Pb and P levels from simulated 1975 certification fuel containing 30 mg of Pb/gal and 2.1 mg of P/gal to 1977 certification fuel contaminant levels of 7 mg of Pb/gal and 0.8 mg of P/gal. Sulfur was maintained constant at a level of 0.02 wt %.

The present laboratory research extends the study of the effects of Pb and P fuel contaminants on Pt–Rh TWCs. The detrimental effects of S on the performance of TWCs have been reported previously (*11*) and will not be dealt with further. Thus, the purpose of the present research was to determine the activity and durability of Pt–Rh TWCs as a function of Pb and P poisoning, thermal aging, and Pt–Rh catalyst composition.

Experimental

Catalysts. The TWC formulations contained Rh as the selective NO reduction component, Pt as the hydrocarbon and CO oxidation component, and proprietary base metal promotors. TWCs identified in Table I were prepared on Corning EX-20 monolithic supports. The catalyst supports had a cell density of 49 square cells/cm^2. All of the TWCs had similar total noble metal loading (Pt + Rh = 0.2 wt %) but differing Pt/Rh ratios. The fresh BET area of these catalysts varied from 14.6 to 17.0 m^2/g. Catalyst buttons, 1.9 cm diameter × 1.3 cm long, were used in these studies.

Apparatus and Procedure. *Pulse-Flame Reactor Durability Testing.* The procedure for durability testing of TWCs using pulse-flame reactor techniques is given in ref *10*; a more detailed description of the pulsator apparatus and instrumentation for the exhaust stream analysis is reported in ref *12*. The simulated mileage accumulation of pulsator durability utilized lead-sterile isooctane and simulated fuels containing

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Table I. Description of Catalysts[a]

catalyst ident	Pt + Rh, wt %	Pt/Rh	BET area, m^2/g
M-268B	0.2	11/1	fresh: 16
M-268D	0.2	11/1	fresh: 16
M-261A	0.2	19/1	fresh: 16.0 aged: 13.7 (17 400 miles/fuel D)[b] 10.8 (21 100 miles/fuel F) 10.4 (17 500 miles/fuel E)
M-265B	0.2	5/1	fresh: 17.0 aged: 12.3 (16 500 miles/fuel D) 14.7 (18 200 miles/fuel F) 12.4 (18 600 miles/fuel E)

[a] Contain base-metal oxide (promoter). Supported on Corning EX-20 Monolith, 49 square cells/cm^2. [b] Description of fuels given in Table II.

Table II. Contaminant Levels in Simulated Fuels for Pulsator-Aged Catalysts

fuel[a] designation	Pb,[b] mg/gal	P,[c] mg/gal	fuel[a] designation	Pb,[b] mg/gal	P,[c] mg/gal
A[d]	0	0	D	6	0.8
B	0	0.9	E	60	1.2
C	1	0.8	F	5	8.2

[a] Isooctane containing 0.03 wt % S in addition to the indicated amounts of Pb and P. [b] From "TEL Motor Mix" containing tetraethyllead, ethylene dichloride, and ethylene dibromide in an atomic ratio of Pb:Cl:Br = 1:2:1. [c] From cresyl diphenyl phosphate. [d] S-, Pb-, and P-free isooctane.

Table III. Conditions for Durability Testing of Three-Way Catalysts on Pulse-Flame Reactor

	feed gas compositions	time duration, %
cycle A	NO = 500 ppm CO = 1.5% O_2 = 0.8% HC = 2000 ppmC	~83.3 (T > 400 °C)
cycle B	NO = 500 ppm CO = 1.5% O_2 = 2% HC = 2000 ppmC	~16.7 (T < 400 °C)

fuel: isooctane or (isooctane + Pb + S + P)

temperature cycle	
T, °C	time duration, %
340	16.7
515	77.0
730	6.3

space velocity: 40 000 h^{-1}
simulated mileage accumulation: ~5000 miles/week (168 h)

the Pb and P contaminant levels listed in Table II.

In the laboratory catalyst aging procedure the catalyst is exposed to feed gas compositions and temperature cycles shown in Table III. The low-temperature oxidizing cycle B simulates the cold-start exhaust conditions, and the high-temperature cycle A is intended to simulate high acceleration modes of operation. The simulated mileage calculations are based on a 30 mph [or 5000 miles/week (168 h)] steady-state vehicle operation at a nominal 40 000 h^{-1} space velocity.

Steady-State Activity and Selectivity. Following the pulsator durability, the catalytic steady-state activity was measured at 550 °C in a separate flow reactor system described previously (*10*) operating at 60 000 h^{-1} space velocity with a simulated gas mixture containing 20 ppm of SO_2. The synthetic gas mixture contained NO, CO/H_2 = 3, C_3H_6/C_3H_8 = 2, SO_2, CO_2, and H_2O in N_2. A detailed gas mixture composition is given in Table IV. Propylene and propane represented fast-burning and slow-burning hydrocarbons, respectively.

Table IV. Feed Gas Composition of Simulated Gas Mixture

component	vol, %	component	vol, %
NO	0.1	C_3H_8	0.015
O_2	0.6–1.0	H_2O	10
CO	1.2–2.0	CO_2	10
H_2	0.4–0.7	SO_2	0.002
C_3H_6	0.03	N_2	balance

Table V. Effect of Thermal and Thermal plus Chemical Aging on Performance of M-268B Catalyst[a]

			% conversion at peak temp in durability cycle			
			730 °C		820 °C	
R		fresh	iso-octane	fuel D	iso-octane	fuel D
~1.05	net NO	98	96	84	96	86
	NH_3[b]	0	0	0	0	0
	gross NO	98	96	84	96	86
	CO	97	98	100	94	98
	HC	94	95	84	90	86
1.8	net NO	80	74	23	69	44
	NH_3[b]	20	20	43	28	32
	gross NO	100	92	40	96	64
	CO	37	38	40	40	—
	HC	64	69	34	72	59
$T_{80\%}$, °C		225	—	280	275	280

[a] Pretreatment: 25 000 simulated miles on pulsator. Durability fuel: thermal aging, lead-sterile isooctane (fuel A); thermal + chemical aging, fuel D containing 6 mg of Pb + 0.8 mg of P + 0.03 wt % S/gal of isooctane. Activity measurements in flow reactor: space velocity = 60 000 h^{-1}; T = 550 °C; simulated exhaust gas containing 20 ppm of SO_2. [b] As percent NO converted.

The activity and three-way selectivity of the catalysts are reported as percent conversion of NO, CO, and HC as a function of the redox ratio, R, of the reacting gas mixture. (R is a measure of the gas mixture stoichiometry of reducing to oxidizing components and is determined as follows: $R = [CO + H_2 + 3nC_nH_{2n} + (3n + 1)C_nH_{2n+2}]/(NO + 2O_2)$. Thus, $R = 1$ corresponds to a stoichiometric gas mixture, while $R > 1$ represents an overall reducing gas mixture.)

Results and Discussion

Susceptibility of TWCs to Trace Levels of Pb. In order to differentiate thermal deactivation from combined chemical and thermal deactivation of TWCs, M-268B catalysts were durability tested for 25 000 simulated miles on pulsators burning (a) isooctane (fuel A) and (b) simulated 1977 certification fuel (fuel D). The peak temperature of the pulsator aging cycle (Table III) was varied from 730 to 820 °C for two separate 25 000-mile aging tests.

The steady-state activity results are shown in Table V for the redox ratio ($R \simeq 1.05$) corresponding to the maximum simultaneous three-way conversion of NO, CO, and HC (NO and HC conversion crossover) and for R equal to 1.8 corresponding to 2.8% rich of stoichiometry. At R = 1.8, the net NO and HC conversions decrease after aging in the presence of fuel contaminants when compared to contaminant-free isooctane at either temperature. The conversion of CO was not affected by the fuel contaminants in these tests.

The benefits achievable by decreasing Pb contamination (P and S levels constant) are shown in Table VI for a newer

Table VI. Activity of M-268D Pulsator-Aged Catalysts at Trace Lead Levels[a]

R		% conversion: fuel D (6 mg of Pb/gal)	% conversion: fuel C (1 mg of Pb/gal)
~1.05	net NO	91	97
	NH_3[b]	0	0
	gross NO	91	97
	CO	99	98
	HC	92	94
1.8	net NO	70	77
	NH_3[b]	20	20
	gross NO	87	96
	CO	45	32
	HC	53	59

[a] Pretreatment: 25 000 simulated miles on pulsator using fuel D (6 mg of Pb + 0.8 mg of P + 0.03 wt % S/gal of isooctane) and fuel C (1 mg of Pb + 0.8 mg of P + 0.03 wt % S/gal). Activity measurements: flow reactor with simulated exhaust gas containing 20 ppm of SO_2; T = 550 °C; space velocity = 60 000 h^{-1}. [b] As percent NO converted.

generation M-268D catalyst having the same precious metal loading and Rh content (Pt/Rh = 11) as the former M-268B catalyst. When exposed to fuel at the lower Pb level of 1 mg of Pb/gal for 25 000 simulated miles of pulsator aging, the M-268D catalyst yielded 6–7% higher net NO conversion near stoichiometry and at R = 1.8 than when the catalyst was aged using fuel containing 6 mg of Pb/gal. At R = 1.8 the HC conversion also improved ~6% when aged at the lower Pb level. While HC conversion was improved by lower Pb levels, the CO oxidation decreased. This effect will be discussed later. Although improvements in HC and NO_x by 6–7% do not seem very large on an absolute basis, they are quite significant in terms of unconverted NO and HC. For example, a 6% increase in net NO conversion near stoichiometry reflects a threefold decrease in the unconverted NO, i.e., from 9 to 3%.

The effects of thermal aging at somewhat higher cycling temperatures are beneficial during rich excursions of TWCs. Aging of the M-268B catalysts at the higher peak temperature of 820 °C (instead of 730 °C) improved the net NO and HC conversion (Table V). For example, at R = 1.8 the net NO conversion increased 21% (from 23 to 44%) and the HC conversion improved 25% (from 34 to 59%) when cycled to peak temperatures of 820 °C rather than 730 °C. X-ray fluorescence analysis of the aged catalysts indicated 0.14 and 0.10 wt % Pb retention at 730 and 820 °C, respectively. Contaminant retention of Pb increases with increasing catalyst temperature in the temperature range 350–760 °C (*5*). The catalyst poisoning mechanism proposed by McArthur (*13*) for automotive catalysts predicts that contaminant composition on the catalyst varies with temperature and that contaminant retention decreases as the temperature approaches the values where PbO has an appreciable vapor pressure. For example, PbO has 0.1 Torr vapor pressure at 850 °C (*14*). Thus, the improved NO and HC conversions achieved at the higher cycling temperature of 820 °C are attributed to lower retention of Pb.

The poisoning of Pt by sulfur species in a reducing atmosphere leaves Rh as the major active component (*11,15*). Therefore, during rich operation (R = 1.8, for example) Rh is primarily responsible for the conversion of NO to N_2 (*16–18*), while also being a good steam-reforming catalyst (*1*). Thus, the significant decreases in net NO and HC conversions in the rich region are attributed to the lower availability of active Rh on the aged TWC. On the other hand, near stoichiometric conditions ($R \simeq 1.05$) where SO_2 poisoning on Pt becomes less significant, and in the absence of H_2, the Pt sites of the TWC contribute significantly toward higher net NO conversion and HC oxidation (*15*). The present steady-state results indicate that for pulsator-aged Pt/Rh catalysts having relatively low Rh content, the current fuel Pb levels have a significant effect.

Extent of Poisoning vs. Catalyst Composition. The effects of various Pb and P contaminant levels were determined for two TWC formulations containing the same total precious metal loadings (0.2 wt %), but differing in the Pt/Rh ratio. A relatively low Rh-content catalyst, M-261A, and a relatively high Rh-content catalyst, M-265B, contained ratios of Pt/Rh = 19/1 and 5/1, respectively. These catalysts were pulsator aged for 15 000 to 20 000 simulated miles using simulated fuels described in Table II: (a) base-line simulated 1977–1978 certification fuel D, (b) fuel B which is fuel D minus Pb, (c) fuel E which is fuel D with 60 mg of Pb/gal, and (d) fuel F which is fuel D with 8.2 mg of P/gal. BET surface areas of the catalysts aged using the various fuels are shown in Table I. The aged catalysts have retained sufficient surface areas to eliminate any excessive deactivation that could be attributed to sintering of the catalyst caused by overheating.

The effects of Pb levels on the two catalysts are shown as a function of redox ratio and air/fuel ratio (A/F) for net NO conversion in Figure 1, for HC conversion in Figure 2, and for

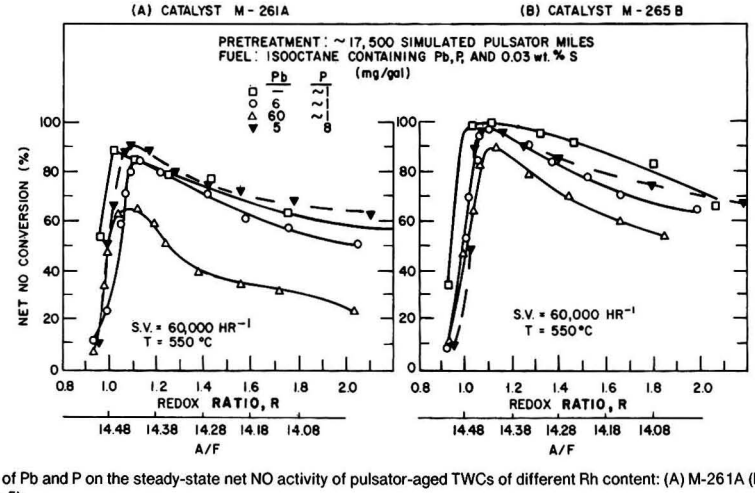

Figure 1. Effects of Pb and P on the steady-state net NO activity of pulsator-aged TWCs of different Rh content: (A) M-261A (Pt/Rh = 19) and (B) M-265B (Pt/Rh = 5)

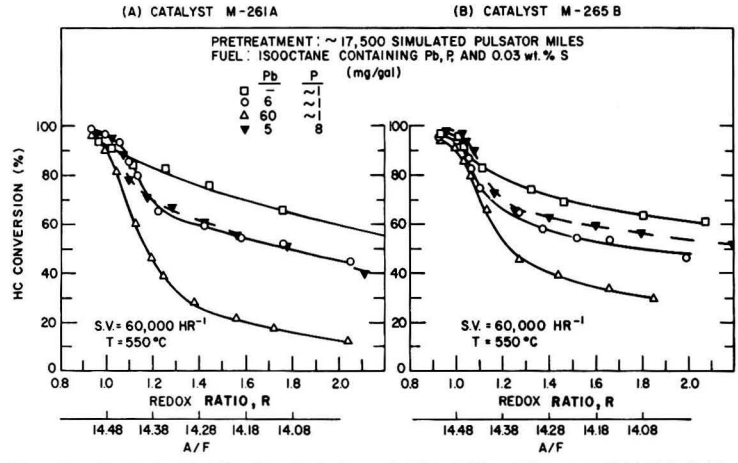

Figure 2. Effects of Pb and P on the steady-state HC activity of pulsator-aged TWCs of different Rh content: (A) M-261A (Pt/Rh = 19) and (B) M-265B (Pt/Rh = 5)

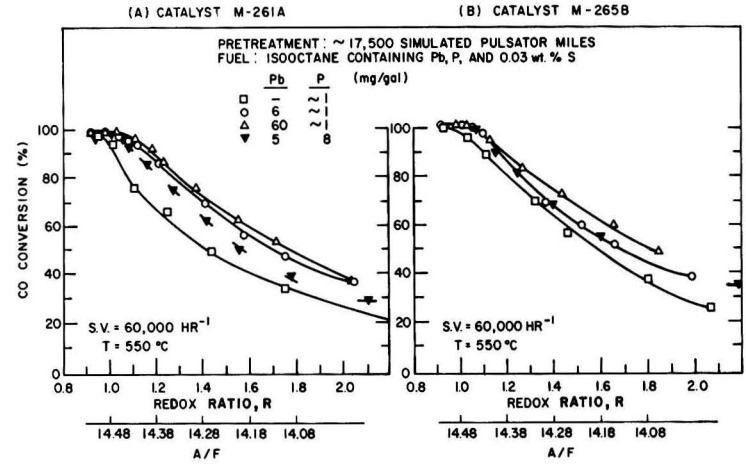

Figure 3. Effects of Pb and P on the steady-state CO activity of pulsator-aged TWCs of different Rh content: (A) M-261A (Pt/Rh = 19) and (B) M-265B (Pt/Rh = 5)

CO conversion in Figure 3. The net NO conversion of both catalysts decreases over the range of R values with increasing amounts of Pb present in the fuel. The low Rh-containing TWC shown in Figure 1A is severely poisoned at levels of 60 mg of Pb/gal. For example, the net NO conversion over the M-261A catalyst decreases 24% (90 to 66%) near stoichiometry at $R \simeq 1.05$ and the net NO conversion decreases by 34% (65 to 31%) at $R = 1.8$ by increasing Pb content from 0 to 60 mg/gal. By comparison, for the M-265B TWC containing more Rh the poisoning effect by higher Pb levels is much less pronounced (Figure 1B). For example, the net NO decreases 15% (97 to 82%) at $R \simeq 1.05$ and 17% (82 to 55%) at $R = 1.8$.

The hydrocarbon conversion over both TWCs is affected to an even greater extent by the 60 mg of Pb/gal fuel, especially during rich operation. The HC conversion at $R = 1.8$ over the M-261A and M-265B TWCs decreases by 47% (63 to 16%) and 33% (64 to 31%), respectively, at the higher Pb levels when compared to the Pb-free fuel. Near stoichiometric conditions, where poisoning of Pt by S is minimal and Pt contributes to the HC conversion, the differences in HC conversion over the two catalysts and deterioration in HC activity to higher leaded fuel are smaller.

Another criterion for judging catalytic performance is to compare the temperature required to reach 80% conversion of the limiting reactant HC. (As shown in Table IV, the ratio of C_3H_6/C_3H_8 is 2/1. One can discriminate catalyst efficiency by the oxidation of the more difficult-to-oxidize C_3H_8.) The temperature required for three-way conversion of NO, CO, and HC decreases significantly as Pb levels are lowered. The higher Rh-containing catalyst also lowers this temperature for each of the fuels investigated, as well as improving the net NO activity.

CO oxidation over the TWCs is affected to a lesser extent by increased Pb poisoning than for HC oxidation, but CO conversions improve slightly with increased Pb levels, as shown in Figure 3 and mentioned previously in Table VI for the M-268D catalyst. The M-261A and M-265B catalysts show higher CO conversion activities of about 16% at $R = 1.8$ for 60 mg of Pb/gal levels when compared to the Pb-free fuel. Since the oxidation of hydrocarbons is a more demanding reaction

requiring multiple adjacent active sites, poisoning by Pb affects the HC oxidation activity severely. In the rich A/F ratio region where CO + HC ≥ O_2, oxygen is partitioned between HC and CO. Any decrease in HC conversion may release equivalent oxygen for a stoichiometric increase in CO oxidation.

An order of magnitude increase in the P content of the fuel has no poisoning effect, as shown by the dashed lines in Figures 1 and 2 for the M-261A and M-265B catalysts. In fact, the net NO and HC conversion are slightly improved by the relatively high P levels for the fuels that contained similar Pb and S contaminant levels. The catalytic activities following aging at 8 mg of P/gal levels are slightly better than those aged with 6 mg of Pb/gal. The small improvement in net NO conversion is attributed to the formation of stable, inert lead phosphate, $Pb_3(PO_4)_2$. Fuel containing 8 mg of P (0.26 mg-atom of P)/gal and 5 mg of Pb (0.024 mg-atom of Pb)/gal would have a tenfold atomic excess of P to Pb. The excess P could conceivably neutralize poisoning by Pb to some extent by the formation of lead phosphates. $Pb_3(PO_4)_2$ was indeed identified previously on catalysts by X-ray diffraction analyses (*5,13*).

Concluding Remarks

For a large scale practical application of three-way catalytic converters, the Pt/Rh ratio should be close to the mine ratio of 17/1. Catalysts containing Rh considerably higher than that deemed practical, because of the limited Rh supply, were capable of lowering NO_x and hydrocarbon emissions even in the presence of relatively high Pb contamination. The laboratory performance of TWCs having a more realistic Rh content improved significantly when Pb contamination was reduced 90% from the 1975 levels near 60 mg of Pb/gal to levels of 6 mg of Pb/gal, representative of current contamination in marketed unleaded fuel. However, these laboratory tests simulating automotive exhaust conditions revealed that these TWCs were sensitive to even these trace levels of Pb. When Pb contamination was reduced further, the laboratory studies indicated that the deactivation of the TWCs by Pb was further alleviated.

In these studies Pt–Rh TWCs were not sensitive to trace levels of P (0.8 mg of P/gal) found in current unleaded fuels. However, when the fuel contained a large atomic excess of P to Pb, the possible formation of nonpoisonous, stable lead phosphates minimized poisoning of the Rh to some extent.

Catalyst deactivation by Pb was also decreased when catalysts were operated at higher temperatures due to lower Pb accumulation on the catalyst by volatilization of PbO. However, catalyst operation at elevated temperatures may make them more suceptible to thermal deactivation by overheating from the engine exhaust. Therefore, a satisfactory compromise between improved performance from lower Pb retention and the potential risk of thermal deactivation must be reached.

Acknowledgments

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Effects of Sodium Chloride on Limestone Calcination and Sulfation in Fluidized-Bed Combustion

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Considerable attention is being focused on fluidized-bed combustion of coal as a result of its potentially higher efficiency and low capital costs (*1*). In the FBC process, coal is burned at 850–900 °C and 10^5 to 10^6 Pa pressure in a fluidized bed of a partially sulfated solid SO_2 sorbent such as limestone or dolomite. Steam generation in boiler tubes immersed in the bed removes part of the heat of combustion. The limestone bed material both transfers heat to the boiler tubes and, by reacting with the sulfur-containing gas, captures the potentially harmful SO_2 released from the coal.

At the stated operating conditions, after calcination, CaO in the limestone or dolomite reacts with SO_2 and O_2 to form stable $CaSO_4$, leaving exhaust gases that are relatively free of sulfur.

Limestones and dolomites are being extensively evaluated (*2*) as fluidizing materials because of their high calcium con-

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■ A laboratory investigation of the interaction of sodium chloride with natural limestones during calcination and sulfation has been performed. Reactions were carried out at 850 °C in a synthetic flue gas consisting of 0.3% SO_2, 5% O_2, 20% CO_2, and the balance nitrogen. Results show that the presence of salt induces structural rearrangement in the stones that can lead to an optimum pore distribution for reaction with SO_2/O_2 mixtures. The salt effect involves the presence of a liquid phase that increases the ionic diffusion and mobility of the system, enhancing calcination, enhancing crystallization of CaO, and creating a pore structure permeable to reactant gas diffusion. Application of NaCl addition to fluidized-bed coal combustion would increase the sulfur capacity of unreactive limestone and would reduce the quantity of limestone needed and the amount of solid waste produced in meeting SO_2 emission standards.

tent and thus high capacity for SO_2 removal, their low cost, and their widespread availability. Owing to the low price of naturally occurring limestones, the sulfated product possibly can be disposed of as solid waste without regeneration and recycling. Regeneration of the limestone or dolomite is also a possibility (*3*). The major disadvantage of using a natural limestone or dolomite without improving its SO_2-removal capability is the environmental impact of extensive quarrying and the disposal of large quantities of solid waste material.

Any process would be advantageous that would reduce the sorbent requirement—for example, by increasing the reactivity of the limestone or dolomite sorbent. Some high-calcium limestones do not fully react to form $CaSO_4$. If the amount of $CaSO_4$ formed in such stones could be substantially increased, the stones would become more effective sorbents and the dependence on naturally reactive stone could be reduced or eliminated. Obviously, both the amount of material required and the amount of waste produced would be reduced by using more of the available calcium in the stone. For example, by increasing conversion from 25 to 40% for an 80% $CaCO_3$ limestone, the amount of stone needed to remove 85% of the sulfur emitted during combustion of coal containing 4% sulfur is reduced by almost one-half.

The use of sodium chloride as an enhancement agent for sulfur capture in fluidized-bed combustion was reported earliest for the combustion of oil shales in a shale–limestone bed (*4*). In pilot plant studies (*5, 6*), adding salt to fluidized-bed coal combustors was demonstrated to be a way of decreasing the levels of SO_2 in off-gases. The reactivity of limestones with SO_2 was found to be affected by many variables, including the sodium content of the natural stone and the method of calcination (*7*).

Inorganic salts have been used in the lime industry to alter the physical properties of calcined limes for many years (*8–11*). Such physical effects on limestone calcines appear to form the basis for the enhanced ability of stones to react with sulfur dioxide.

The present study was initiated to investigate this interaction, with particular regard to using limestones more efficiently to reduce environmental contaminants in FBC off-gas.

Laboratory studies were performed on the interaction of inorganic salts with limestones during calcination and sulfation in order to verify the positive enhancement effects and to obtain a more complete understanding of the process and the optimization of its effects. Sodium chloride was chosen as the additive to be investigated most thoroughly, since it was used in the successful FBC runs mentioned above (in ref *5* and *6*) and is a natural component of limestones. It has also been shown in laboratory studies (*12–18*) to have dramatic effects on the decomposition temperatures and other properties of carbonates.

Experimental

Naturally occurring limestones were used throughout this work in order to note the effects of composition and structure on reactivity. Table I lists compositions in weight percent for limestones referred to in the figures of this paper. The first two digits of the ANL number designation refer to the nominal $CaCO_3$ content of the stones. The reactions studied, both calcinations and sulfations, were carried out in shallow quartz boats (in horizontal tube furnaces), with a single layer of limestone particles exposed to controlled atmospheres that were designed to simulate flue gas. The temperature of reaction was kept at 850 °C, which is a typical fluidized-bed coal combustor operating temperature. The calcination gas composition was 5% O_2, 20% CO_2, and the balance N_2 flowing at a rate of 500 cm^3/min. For sulfation reactions, 0.3% SO_2 was added to this mixture, and reaction was allowed to proceed to near completion.

The 1-g samples of 18–20 mesh limestone were periodically weighed to monitor the progress of the reaction and were analyzed for sulfate at the conclusion of the 6-h reaction period for comparison with the sulfation values indicated by the weight change measurements. A mercury porosimeter was used to generate pore distribution data, as well as surface areas and average pore diameters, on 1-h-calcined samples and on stones that had undergone other treatments. A scanning electron microscope was also used to provide visual references for determining structural changes that might occur. Baker reagent grade NaCl was used throughout the investigation. The salt was generally introduced by complete evaporation of an aqueous slurry onto the raw stones before calcination to obtain a uniform distribution on the particle surface and accessible pore space and thus ensure intimate contact with the limestones.

Results and Discussion

Figures 1 and 2 show sulfation reaction curves for several limestones, untreated (Figure 1) and treated with 2 wt % NaCl (Figure 2). The effects of treatment with salt are apparent—an increased initial slope of the sulfation curves and a greater amount of sulfation in the same time interval, as compared with the raw untreated stones. These data represent simultaneous calcination and sulfation, a situation that presumably exists in a fluidized-bed coal combustor. However, for experimental purposes, the effects of calcination alone can be separated from the effects of the sulfation reaction by treating the material with salt and then precalcining the material for 1 h. This was done for all subsequent reactions to remove the effects of at least that one variable (slow or incomplete calcination).

Figure 3 is a bar graph showing the effect of NaCl at different concentrations on the percentage conversion of available CaO to $CaSO_4$ for precalcined stones. The reactivity reached a maximum with a salt content near 0.5 wt % for most of the stones, as was concluded from the extent of reaction at several different salt concentrations. The reactivity begins to decrease as NaCl amounts larger than 0.5 wt % are added due to loss of the surface area. The point where reactivity begins to decrease appears to be related to the amount of impurities present in a stone.

Figure 4 is a typical set of porosity curves showing the effect on pore distribution of NaCl during calcination. This particular stone (ANL-9501) has a low impurity content (3 wt %), and the shifts observed in average pore diameter with different NaCl additions are smaller than for pure $CaCO_3$ (calcite), but greater than for a stone with impurity levels of 10% or more.

Table I. Compositions of Representative Limestone Samples

designation	$CaCO_3$, %	$MgCO_3$, %	Fe_2O_3, %	Al_2O_3, %	SiO_2, %	Na_2O, %	K_2O, %
ANL-8001	80.4	3.5	1.24	3.18	10.34	0.23	0.72
ANL-8101	81.6	11.6	0.86	0.19	1.86	0.10	0.07
ANL-8701	87.0	1.20	3.4	2.0	7.1	0.13	0.19
ANL-8901	89.8	2.15	0.66	1.04	4.0	0.10	0.19
ANL-9201	92.6	5.33	0.20	0.42	1.26	0.10	0.02
ANL-9501	95.3	1.32	0.09	0.25	0.77	0.03	0.06
ANL-9601	96.0	3.57	0.23	0.01	0.18	0.04	0.01
ANL-9701	97.8	0.6	0.10	1.8	0.2	0.25	0.47
calcite spar	100.0	0	0	0	0	0	0

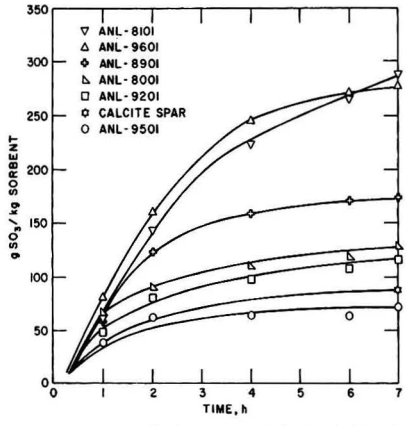

Figure 1. Reaction curves for limestones calcined and sulfated simultaneously at 850 °C for 5 h in 0.3% SO_2, 5% O_2, 20% CO_2, balance N_2

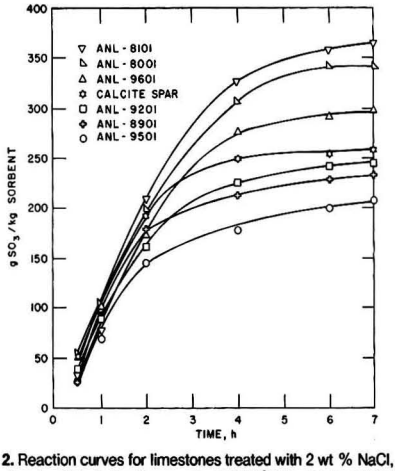

Figure 2. Reaction curves for limestones treated with 2 wt % NaCl, then calcined and sulfated simultaneously at 850 °C for 5 h in 0.3% SO_2, 5% O_2, 20% CO_2, balance N_2

The inherent porosity in a lime is produced as a result of the evolution of CO_2 at high temperature without any change in gross physical dimensions. As salt is added, the majority of pores have increasingly larger diameters, as indicated by the midpoint of the rise in the porosity curve gradually shifting to larger pore diameters as salt content goes up.

This structural change can be readily seen in scanning electron microphotographs of this same stone. Figure 5 shows

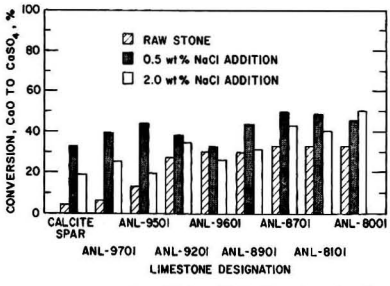

Figure 3. The effect of 0.5 and 2.0 wt % NaCl treatment on limestone subsequently precalcined and sulfated at 850 °C for 5 h in 0.3% SO_2, 5% O_2, 20% CO_2, balance N_2

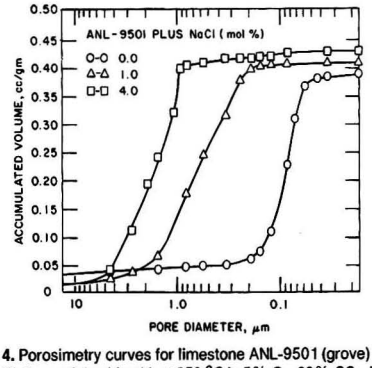

Figure 4. Porosimetry curves for limestone ANL-9501 (grove) treated with NaCl, then calcined for 1 h at 850 °C in 5% O_2, 20% CO_2, balance N_2

that the increasing pore diameters due to salt addition would allow sulfation to occur for a longer time before the formation of an impervious shell of $CaSO_4$. Despite the fairly large pore sizes of the untreated stone, the unreacted material is sealed off when the $CaSO_4$ reacts first with the particle surface. When salt is present, recrystallization and rearrangement of the CaO and $CaSO_4$ maintain gaseous permeability for much longer periods. Earlier studies (*19*) showed that there is a minimum pore size for effective sulfation. Pores smaller than 0.3 μm are closed off rapidly by $CaSO_4$ (*20*), which has a larger molar volume than does the original $CaCO_3$. The presence of trace amounts of surficial liquid produced by localized melting of NaCl with some dissolved CaO and $CaSO_4$ is proposed as the basic mechanism for initiation of these structural changes as illustrated in Figure 6. With increased ionic mobility there is pore growth, as well as crystallite growth of both CaO and $CaSO_4$, throughout the reaction as long as residual salt remains in the particle.

The structures developed with NaCl are very similar to

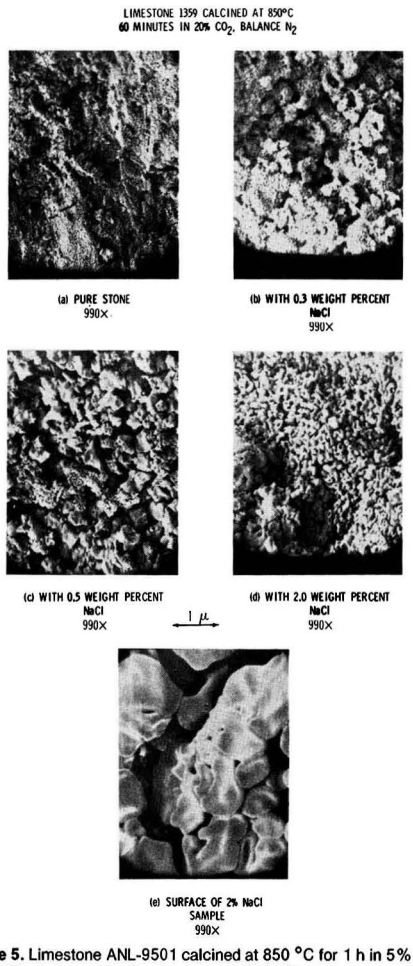

Figure 5. Limestone ANL-9501 calcined at 850 °C for 1 h in 5% O_2, 20% CO_2, balance N_2 after treatment with NaCl

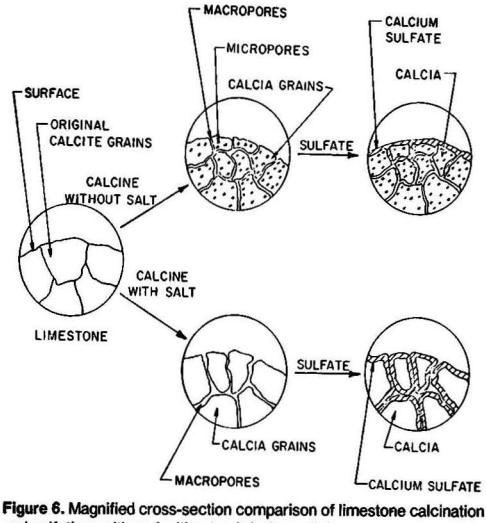

Figure 6. Magnified cross-section comparison of limestone calcination and sulfation, with and without salt (schematic)

those for high-temperature calcined limes. This high-temperature effect is referred to as sintering, wherein the calcia grains grow together at a rate directly related to temperature. Stones fired at temperatures greater than 1200 °C are called "dead-burned" because of their inactivity with respect to hydration. This is due to their extremely low surface area, high crystallinity, and unconnected pore space. The porosity curves show the same trend of increasing pore diameter with increasing temperature as for stones with increasing salt content at a single temperature. This sintering effect is essentially a reflection of the ionic mobility within the lattice structure of the calcine. Additives have been most frequently assumed to control defects in diffusional sintering, and have not been commonly interpreted to have effects as liquid (*21*). It was felt that sufficient liquid was necessary to completely wet the boundary of grains before the effect would be noticeable.

Some work on the BeO–CaO system shows that the volume fraction of liquid necessary to greatly enhance sintering rates can be less than was formerly thought (*22*). The ranges of effective additive content varied from 0.01 to 0.05 mol %.

From the above discussion, we arrive at the conclusion that the effects of NaCl in limestones are to accelerate the rates of sintering and crystal growth during both calcination and sulfation. It is believed that this is primarily due to the presence of a liquid phase that increases ionic mobility and diffusion.

Since NaCl has the effect of an impurity, it is necessary to observe the effect of salt on impure limestones as well as on pure limestones to expand our understanding to more commonly occurring natural limestones and dolomites, which usually contain appreciable amounts of materials other than $CaCO_3$. These incorporated impurities might or might not affect the reactivity of the calcine with SO_2/O_2. On this basis, the program included a study of the sulfation of a broad range of limestone compositions.

Figure 7 shows the effects of salt on calcite spar (naturally pure $CaCO_3$) during sulfation. The depth of penetration of sulfate formation is much greater for salt-treated stones than for untreated ones. The photograph illustrates the enlarged pore structure and the formation of $CaSO_4$ on the grain surfaces, internally as well as externally.

Figure 8 is a graphic representation of data, for 27 different stones, illustrating the effect of pore diameter on sulfation reactivity. Average pore diameters were calculated from surface area pore volume measurements on a mercury porosimeter, using a model of a right circular frustrum for pore shape. The distribution of points shows that initially, as pore diameter increases, reactivity increases, reflecting the previously mentioned minimum effective pore size of 0.3 μm. As the average pore diameter increases further, gaseous permeability increases. However, surface area decreases continually and eventually becomes the controlling factor over permeability; the reactivity decreases with further salt addition (i.e., further pore enlargment). The maximum theoretical conversion to $CaSO_4$, which is limited by pore volume, is ~70% of the available CaO. Most stones studied achieved 50% or greater conversion at low salt concentrations before pores were sealed by $CaSO_4$.

From this type of plot, potentially unreactive stones can be identified. Also, the desirability of adding salt for enhancement and the relative quantities of salt to be added for application to fluidized-bed coal combustors can be deduced.

Summary and Conclusions

The treatment of limestones with NaCl before calcination and sulfation results in structural changes—in particular, pore enlargement that enhances the reaction with SO_2/O_2. Increasing the concentration of salt results in an initial increase

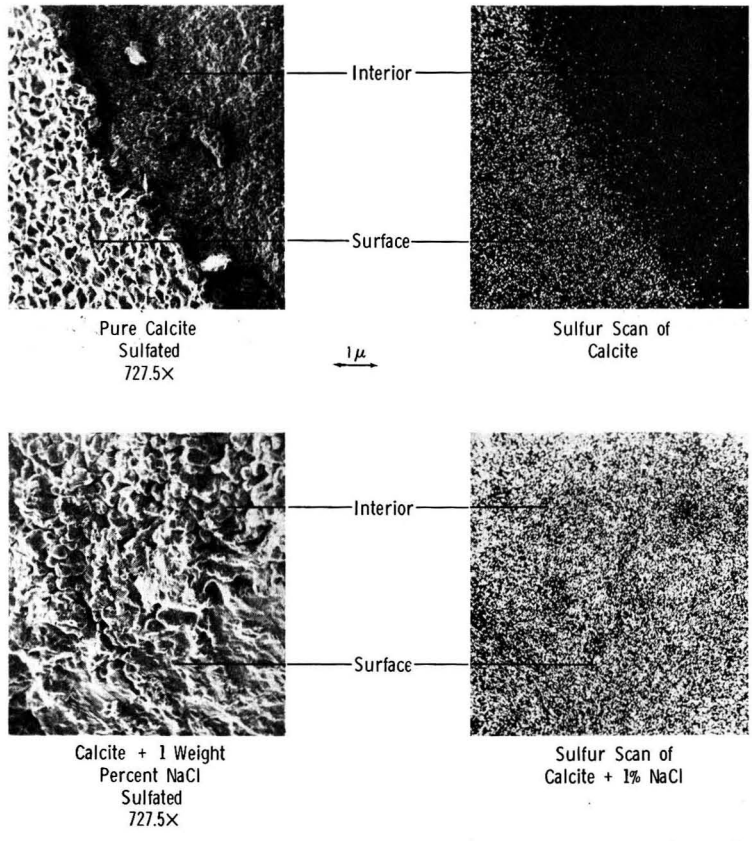

Figure 7. Effect of NaCl treatment on calcination/sulfation of calcite spar at 850 °C for 5 h in 0.3% SO_2, 5% O_2, 20% CO_2, balance N_2

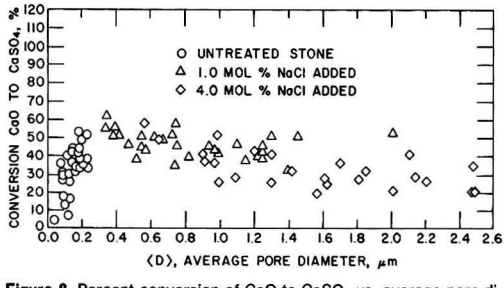

Figure 8. Percent conversion of CaO to $CaSO_4$ vs. average pore diameter (pores ≥ 0.3 μm) for limestones at 850 °C with and without NaCl calcined for 1 h in 5% O_2, 20% CO_2, balance N_2, and sulfated for 5 h with added 0.3% SO_2

in SO_2/O_2 absorption, followed by a decrease in reactivity in most cases due to loss of surface area. In some pure limestones, the effectiveness of the salt is greater and, thus, larger shifts in pore diameter result upon the addition of NaCl.

The effect of salt addition may be duplicated by any means that increases ionic mobility and diffusion. Thus, high temperature can cause either solid–solid sintering, or the formation of liquids that act as accelerators of sintering and result in changes in pore structure (*22*). High CO_2 pressures also result in increased ionic mobility (*23*), thereby improving sulfation under certain conditions. Control of the pore sizes developed during calcination is necessary to achieve maximum sulfation. The sodium chloride data show that at average pore diameters above 0.3 μm, reactivity falls off as long as the structural integrity of the stone is maintained. Any of the techniques suggested above must be predictable and controllable to be effective in FBC.

In fluidized-bed coal combustion, the addition of empirically determined amounts of salt should affect the maximum amount of sulfation for any limestone, regardless of impurity content. By introducing salt during precalcination outside the combustor, possible corrosive effects due to the increased alkali content of the bed material may be eliminated. The effects of aluminosilicate formation between alkalies and coal ash may also reduce the potential corrosiveness of salt addition, as evidenced by the successful use of salt by Pope et al. (*6*). Salts other than NaCl are effective in changing the properties of lime (*8–11*) and may also be effective in enhancing the sulfation properties of limestone in a similar manner.

The effectiveness of salt in FBC will depend on the amount of salt used, as well as the limestone chosen and the combustion conditions of the system. The best reasons for using sulfation enhancement agents are the smaller amounts of stone to reduce the SO_2 emissions and the smaller amounts of solid wastes generated.

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Azaarenes in Recent Lake Sediments

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■ Azaarenes were characterized in several Recent and ancient sedimentary samples and anthropogenic source materials by glass capillary gas chromatography using nitrogen-specific detection, gas chromatography/mass spectrometry, and probe distillation/low voltage mass spectrometry. In lake surface sediments and street dusts, unsubstituted azaarenes containing three to five aromatic rings predominate over the more numerous alkyl homologues. In contrast, azaarenes in fossil organic matter have a much more complex composition, with alkyl azaarenes much more abundant than unsubstituted molecules. In this respect, the azaarenes resemble the PAH composition of these samples. Diazaarenes were apparently also present. An anthropogenic origin for the aza aromatics in the surface sediments is indicated, with street dust as a likely source for some of the sedimentary azaarenes. There is no evidence that natural combustion processes contribute azaarenes to Recent lake sediments.

Aza heterocyclic hydrocarbons (azaarenes) are potentially hazardous environmental contaminants because of their carcinogenic and mutagenic character (*1, 2*). As trace components, azaarenes have been detected in cigarette smoke (*3*), automobile exhaust (*4*), industrial stack effluents (*5*), and urban suspended particulate matter (*6–8*). Petroleum (*9*), shale oil (*10*), coal tar (*11*), and fossil hydrocarbon minerals (*12*) also contain substantial amounts of a very complex and therefore poorly characterized mixture of aza aromatic compounds.

Recently, Blumer et al. (*13*) reported a rich assemblage of azaarenes and their alkylated homologues in two coastal surface sediments. The origin of these compounds was presumed, but not proven, to be natural forest and prairie fires rather than anthropogenic pyrolysis and combustion processes. However, the low voltage mass spectral probe distillation technique Blumer used did not permit identification and quantitation of individual constituents in the complex aza mixture.

Environmental materials containing azaarenes also usually contain polycyclic aromatic hydrocarbons (PAH; *3–13*). This suggests that both compound classes may have common sources and fates in aquatic systems. At EAWAG we have been investigating the geochemistry of PAH in Recent lake sediments (*14–16*), and it was of interest to extend our studies to provide some analogous geochemical information about azaarenes. To do so, glass capillary gas chromatography using nitrogen-selective detection, capillary gas chromatography/mass spectrometry, and probe distillation/low voltage mass spectrometry were applied to characterize azaarene mixtures isolated from Recent lake sediments and other environmental materials. Identification and quantitation of individual constituents were of prime concern. Further emphasis was on a comparison of azaarene distributions in lake surface sediment layers (known to contain primarily anthropogenically derived PAH; *15*) to sediments deposited several hundred years ago (containing few anthropogenic PAHs but several PAHs generated by post-depositional processes; *16*). This paper describes the isolation and characterization of azaarene assemblages in environmental materials and discusses preliminary environmental and geochemical implications of the results.

Experimental

Environmental Samples. Surface sediments (0–10 cm)

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were collected from Lake Zurich and Lake Lucerne, Switzerland, with a grab sampler. Samples of pre-industrial-revolution sediments from Lake Lucerne (80–100 cm; deposited about 400–500 years BP based on a sedimentation rate of 2 mm/year (*15*)) were taken from gravity cores. Previous results show that surface sediments of both lakes contain high concentrations of a wide range of unsubstituted and alkylated PAHs having anthropogenic origins (*15, 16*). In contrast, the older sediments are characterized not only by very low levels of anthropogenic PAH but also by a homologous series of phenanthrenes and perylene that are apparently produced in the sediment during early diagenesis.

The most important present-day anthropogenic source of PAH to surface sediments of the two lakes may be run-off from streets on the adjacent shores (*15*). Street dust is believed to be the prime contributor of PAH to this run-off. Samples of street dusts were swept from heavily traveled asphalt roads in Dübendorf and analyzed for azaarene content. For comparison, a sample of automobile gasoline engine exhaust (collected during a standard dynamometer-type test by the Swiss Federal Institute for Materials and Testing (EMPA), Dübendorf) was also analyzed for azaarenes. Two standard American Petroleum Institute crude oils (Kuwait and South Louisiana) and a sample of Serpiano oil shale (Grenzbitumen-Horizon, Triassic, Switzerland) were examined as representatives of organic-rich ancient sedimentary materials and to compare the azaarene content of ancient materials with Recent materials.

Materials. Silica gel (Merck Kieselgel-40) and alumina (Merck type 1076) were activated overnight at 240 °C, after which their activities were altered with various amounts of water or 1 N HCl. Sephadex LH-20 (Pharmacia Fine Chemicals, Uppsala) was conditioned in benzene–methanol (1:1) before being wet packed into a glass column.

Azaarene reference samples of 2-azafluoranthene, 7-azafluoranthene, 2-azapyrene, 1,2-benzacridine, and 3,4-benzacridine were kindly provided by Rutgerswerke AG (Duisburg, Federal Republic of Germany). Other standard materials were used as obtained from commercial sources (EGA Chemie, Steinheim, F.R.G.; Fluka AG, Buchs, Switzerland).

Isolation of Azaarenes. The isolation procedure is an extension of that briefly outlined by Blumer et al. (*13*), with modifications where necessary to improve recoveries. Dry samples of lake sediment (200–250 g), street dust (60 g), or shale (40 g) were batch Soxhlet-extracted with methylene chloride. Aliquots of concentrated lipid extracts were weighed on a Cahn 4100 electrobalance to estimate the amount of extractable material.

The lipid extracts, or 0.5-g samples of the two crude oils, were dissolved in benzene–methanol (1:1) and charged to a Sephadex LH-20 column (20 g of Sephadex in a 50 × 1.6 cm glass column). The first 50-mL benzene–methanol eluate contained aliphatic and highly pigmented material. Polycyclic aromatic material was collected in a second 50-mL benzene–methanol fraction.

Following evaporation, the aromatic eluate from Sephadex was transferred in pentane to a column of acidic silica gel (8 mL, containing 3% 1 N HCl; 10 × 1 cm column). A 20-mL pentane eluate was discarded, while arenes were eluted sequentially with benzene (20 mL) and 2% methanol in benzene (20 mL). Basic compounds were then recovered by elution with 35 mL of 3% aqueous ammonia in methanol. This fraction was extracted with benzene (3 × 30 mL) in a separatory funnel. The benzene layer was dried over Na_2SO_4 and evaporated.

The basic eluate was rechromatographed on alumina packed over silica (each 4 mL, deactivated with 3% water). A pentane fraction (20 mL) and a methylene chloride eluate (15 mL) were discarded. Azaarenes were collected as two fractions: 20 mL of methylene chloride containing 10% methanol followed by 25 mL of methylene chloride with 40% methanol. These two eluates were combined and evaporated to dryness.

Picric acid (20 mg dissolved in 3 mL of benzene) was added to the material recovered from the silica–alumina chromatography. The benzene was evaporated at room temperature and the residue washed with pentane (3 × 2 mL); the washings were discarded. Any remaining solids were redissolved in benzene, transferred to a separatory funnel, and washed with 5% aqueous ammonia (3 × 30 mL). The organic layer was subsequently washed with water, dried over Na_2SO_4, and evaporated.

The azaarene fraction was further purified by chromatography from alumina (5 mL, 1% water). Any material eluting with 10 mL of pentane was discarded, and the azaarenes were collected by elution with 50 mL of 60% methylene chloride in pentane. A weight of aza material thus obtained was determined by weighing an aliquot on the electrobalance.

Gas Chromatography (GC). Mixtures of azaarenes isolated from the various samples were analyzed by glass capillary gas chromatography using a Carlo Erba Fractovap instrument with a direct on-column injector as described by Grob and Grob (*17*). Detection of nitrogen-containing components was with a Perkin-Elmer nitrogen–phosphorus detector (Model 228-0301). A series of azaarenes ranging from azafluorene to several dibenzacridines (Table I) was best resolved with a glass capillary column (20 m × 0.3 mm i.d.) coated with SP-2340.

Aliquots of azaarene concentrates were injected (1–2 μL in methylene chloride) into the capillary column: both the injector and column were at ambient temperature. After elution of the solvent, the column temperature was rapidly raised to 100 °C and then programmed at 4 °C/min up to 250 °C. Helium carrier gas flow was maintained with a back-pressure of 2.2 atm so that the dibenzacridines would elute within several minutes after reaching the maximum temperature.

Quantitation was by peak area measurements (Spectra Physics Autolab Minigrator) relative to an internal GC standard (octadecanoic nitrile), which was added to the azaarene concentrates immediately before GC analysis. Reported concentrations are corrected for nitrogen detector response of the azaarenes compared to octadecanoic nitrile, analytical recovery efficiencies (determined by replicate analyses of standard mixtures—Table I), and procedural blank content.

Gas Chromatography–Mass Spectrometry (GC–MS). Mass spectral identifications and mass chromatography were carried out with a Finnigan GC–MS (Model 1015D) and interactive data system (Model 6000). The SP-2340 capillary column was directly interfaced to the mass spectrometer by means of a platinum capillary. Gas chromatographic conditions were similar to those described above, except that a conventional Grob-type injector (heated and with septum (*18*)) was used. MS operating conditions were: electron energy, 70 eV; emission current, 350 μA; preamplifier sensitivity, 10^{-8} A/V.

Low-Voltage Mass Spectrometry (LVMS). Information about the degree of alkyl substitution of the azaarene mixtures and evidence for higher molecular weight components not amenable to GC analysis were obtained by the low-voltage (12 eV) mass spectral probe distillation technique described by Giger and Blumer (*19*) and Youngblood and Blumer (*20*). Samples were introduced into the electron source region using closed-end glass capillaries (15 × 2 mm o.d.; 1 mm i.d.) mounted in a low-mass heated probe. To minimize premature loss of low boiling components during introduction, samples were exposed to the fore-vacuum for only 10 s. Scanning over the mass range 120–410 amu every 3 s was initiated immedi-

Table I. Azaarene Response Factors and Recovery Efficiencies

compd	response factor [a]	anal. recovery efficiencies		
		present, μg	found, μg [b]	% recovery
4-azafluorene	0.60 ± 0.04	2.42	0.93 ± 0.33	38
7,8-benzoquinoline	0.64 ± 0.03	2.14	0.81 ± 0.33	38
acridine	0.68 ± 0.03	2.18	0.93 ± 0.16	43
phenanthridine	0.63 ± 0.04	2.23	1.60 ± 0.42	72
5,6-benzoquinoline	0.57 ± 0.02	2.31	1.49 ± 0.36	65
2-azafluoranthene	0.59 ± 0.03	2.09	1.54 ± 0.35	74
7-azafluoranthene	0.71 ± 0.04	2.28	1.59 ± 0.28	70
1-azapyrene	0.71 ± 0.04	2.28	1.85 ± 0.21	81
3,4-benzacridine	0.91 ± 0.06	2.00	1.27 ± 0.29	64
1,2-benzacridine	0.94 ± 0.09	2.58	1.90 ± 0.39	74
1,2,3,4/1,2,5,6-dibenzacridine	1.60 ± 0.16	4.47	2.63 ± 0.60	59
1,2,7,8-dibenzacridine	1.63 ± 0.22	2.36	1.73 ± 0.36	73

[a] Detector response relative to octadecanoic nitrile; ± relative standard deviation for four determinations. [b] Mean ± relative standard deviation for triplicate analyses.

Table II. Characteristics of the Samples

sample	extractable material, mg/g [a]	aliphatic hydrocarbons, mg/g [a]	aromatic hydrocarbons, mg/g [a]	azaarenes, mg/g [a]	org C, %	org N, %
Lake Zurich surface	6.9	0.6	0.07	0.006	5.5	0.9
Lake Lucerne surface no. 1 [b]	2.0	0.1	0.03	0.0008	2.7	0.9
no. 2	1.7	0.1	0.06	0.0005	3.3	0.8
Lake Lucerne 80–100 cm no. 1	1.3	0.03	0.006	NS [d]	2.0	0.6
no. 2	1.0	0.06	0.01	NS	2.1	0.6
street dust no. 1	9.3	1.1	0.6	0.03	ND	ND
no. 2	14.4	2.0	0.9	0.01	ND	ND
auto exhaust [c]	ND [e]	ND	87	2.3	ND	ND
Serpiano shale	30.3	1.9	2.3	0.04	27.5	ND
Kuwait crude	ND	300	39	1.06	ND	ND
South Louisiana crude	ND	350	66	0.4	ND	ND

[a] Gravimetric determination. [b] Samples 1 and 2 are in all cases completely separate samples rather than duplicates. [c] Concentrations/m^3 exhaust. [d] NS, not significant relative to blank. [e] ND, not determined.

ately upon introduction of the probe into the source. Radiative heating from the source caused evaporation of two- and three-ringed azaarenes, after which the probe temperature was raised to about 300 °C to vaporize the remainder of the sample. The resulting 20–50 mass spectra were summed to give the composite mass spectrum for total sample (or any fraction thereof over a desired boiling range). Low-voltage mass spectrometry alone does not provide information selectively about azaarenes, since other components may also give spectra at this low ionizing potential. However, in combination with GC and the nitrogen detector, LVMS does show the presence of azaarenes and gives information about alkyl substitution.

Results and Discussion

Methodology. Most environmental materials contain a variety of classes of nonpolar solvent-extractable organic compounds. As a group, azaarenes apparently represent only a few tenths of 1% of this extractable material (compared, for example, to aliphatic and aromatic hydrocarbons which may be present as 5–10 and 1–5%, respectively, of the extract; Table II). The isolation procedure described here, although requiring many steps, resolves and concentrates the low level azaarenes from more abundant but no less environmentally significant components. Application of glass capillary gas chromatography provides superior resolution of complex aza mixtures compared to previously reported gas (*7, 21*) and high-pressure liquid (*8, 22*) chromatographic analyses. Furthermore, the selectivity of the nitrogen detector helps to discriminate against spurious components that survive the extensive workup or are contaminants from the procedure. For example, using flame ionization detection GC, extraneous peaks interfered with the azaarene determinations. However, these contaminants did not show up using the nitrogen detector or in LVMS. In the case of GC–MS, the azaarenes could be selectively detected using mass chromatographic reconstructions, even in the presence of non-aza contaminants.

Elution volumes for the three adsorption chromatography steps are critical. Substitution of a nitrogen atom for a methyne group of a PAH molecule greatly increases the number of possible isomers for a given molecular weight group, since a number of positions are available for the nitrogen. Elution of these compounds during adsorption chromatography depends on the amount of steric protection of the aza nitrogen and the resulting interaction with the solid adsorbent. For example, 1,2-benzacridine has a more exposed nitrogen and is more strongly adsorbed and retained than the 3,4 isomer. Acridine and 1,2,7,8-dibenzacridine have similar retention times despite large differences in molecular weight and number of aromatic rings. Information about retention of azaarenes on both alumina and silica gel is available elsewhere (*6, 23*). It is therefore imperative that elution volumes be carefully determined for each batch of adsorbent by using a wide range of reference aza compounds and isomer series

Table III. Azaarenes Identified and Their Concentrations in Two Surface Sediments and a Street Dust

peak no.	compd	mol wt [a]	concn, ng/g [b] Lake Zurich surface	Lake Lucerne surface	street dust no. 1
1	4-azafluorene	167	5	0.2	40
2	7,8-benzoquinoline	179	20	0.6	350
3	acridine		27	0.1	32
4	phenanthridine		10	0.3	180
5	5,6-benzoquinoline		31	0.2	185
6	2-azafluoranthene	203	23	0.3	255
7	7-azafluoranthene		27	0.2	265
8	1-azapyrene		20	0.3	210
9	$C_{15}H_9N$ [c]		(33)	(0.2)	(40)
10	3,4-benzacridine	229	45	3.9	525
11	$C_{17}H_{11}N$		(7)	(0.1)	(98)
12	$C_{17}H_{11}N$			(1.0)	(120)
13	1,2-benzacridine		50	0.8	220
14	$C_{17}H_{11}N$		(9)	(0.4)	(170)
15	$C_{17}H_{11}N$		(29)	(1.2)	(74)
16	$C_{19}H_{11}N$	253	(39)	(3.0)	(410)
17			(35)	(1.5)	(300)
18			(90)	(0.3)	(490)
19			(30)	(0.5)	(40)
20			(25)	(2.4)	(90)
21	$C_{21}H_{13}N$	279	(12)	(1.3)	(200)
22	1,2,3,4/1,2,5,6-dibenzacridine		35	5.0	260
23	1,2,7,8-dibenzacridine		37	0.7	56

[a] Molecular weight. [b] Parentheses indicate estimated concentrations based on nearest neighbor identified azaarene. [c] Exact aromatic ring configuration and position of the aza nitrogen could not be determined for compounds assigned molecular formulas.

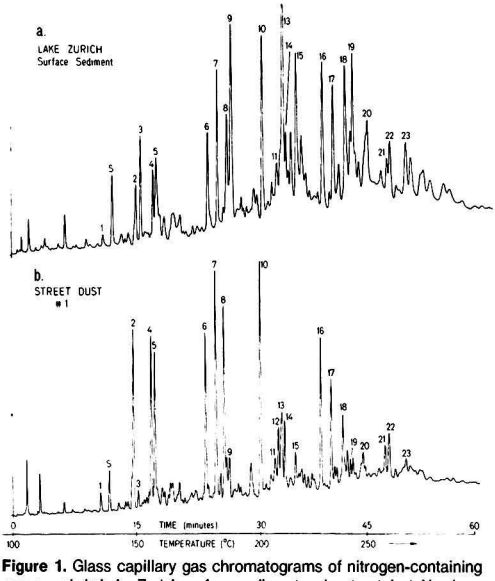

Figure 1. Glass capillary gas chromatograms of nitrogen-containing compounds in Lake Zurich surface sediment and a street dust. Numbers refer to peaks identified in Table III; S = octadecanoic nitrile

having the aza nitrogen at different ring positions. For this investigation, a reference mixture ranging from azafluorene to dibenzacridine (Table I) was used.

Quantitative aspects of the method are shown in Table I in terms of nitrogen-detector response relative to octadecanoic nitrile and analytical recovery efficiencies as determined by capillary GC for a series of reference compounds. Low recoveries for azafluorene, 7,8-benzoquinoline, and acridine are probably due to partial volatilization during the several evaporation steps. Actual samples, however, contain additional lipid material that may act as a carrier and thus improve recoveries of the azaarenes. Recoveries and reproducibilities are adequate for analyses of environmental and geochemical materials.

Characterization of the Azaarenes. The complexity of the azaarene mixtures in the lake surface sediments and street dusts is shown in Figure 1 by capillary gas chromatograms of nitrogen-containing compounds. Major peaks have been assigned on the basis of GC coinjection and GC–MS to unsubstituted aza aromatics (Table III), although the configuration of the aromatic rings (linear, angular, clustered) and the ring position of the aza nitrogen could not always be determined. The numerous minor constituents are alkylated homologues of the unsubstituted species. Estimated concentrations of the identified azaarenes in two surface sediments and a street dust are compared in Table III. No azaarenes were found (detection limit about 0.03 ng of azapyrene/g of dry sediment) in the deep (80–100 cm) Lake Lucerne sediments by either GC or GC–MS. While the Serpiano shale and the two crude petroleums apparently contain an abundance of nitrogen-containing material (Table II), the mixtures of aza aromatics were poorly resolved by GC and none of the azaarenes of Table III could be conclusively identified. Further fractionation, such as by high-pressure liquid chromatography (HPLC), of the azaarenes extracted from the fossil samples prior to GC analysis would be necessary. The automobile exhaust contained aza aromatics over a much lower boiling range, primarily quinoline and alkylquinolines.

The resolution of the capillary column provides an opportunity to evaluate changes in environmental distributions of individual aza compounds. For example, acridine is present in the Lake Zurich sediment as 40% of the three-ringed compounds (Table III). But in the Lake Lucerne sediment and street dust, acridine is a minor (6%) constituent of this group. The reverse is true for 7,8-benzoquinoline. Levels of 3,4- and

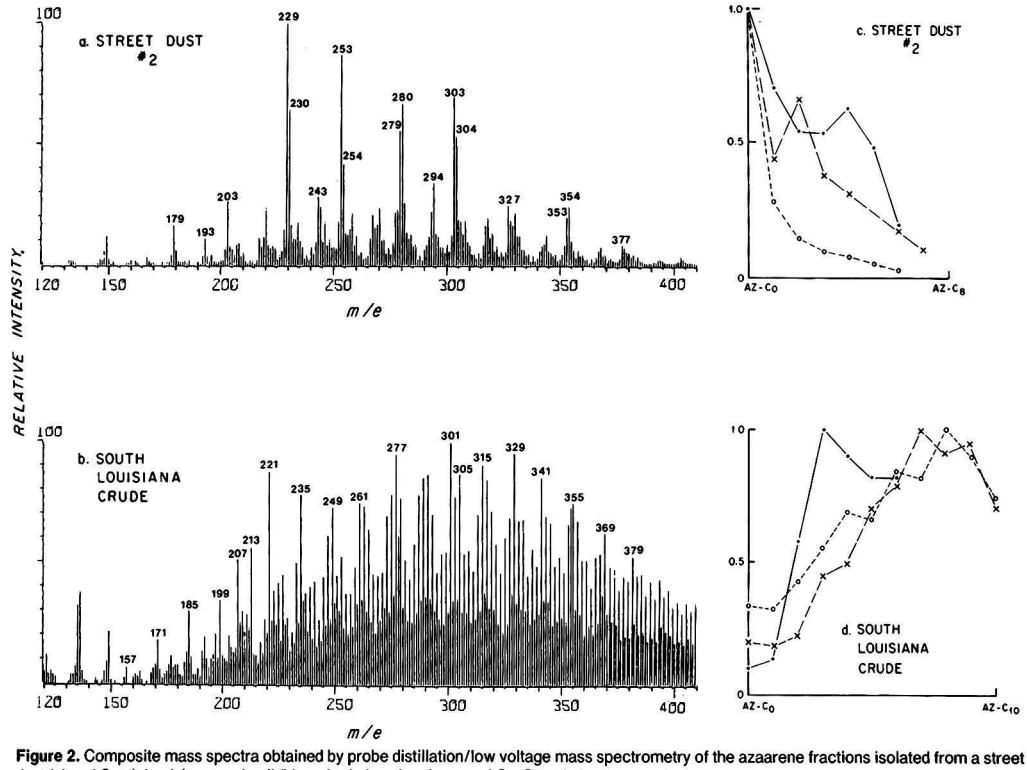

Figure 2. Composite mass spectra obtained by probe distillation/low voltage mass spectrometry of the azaarene fractions isolated from a street dust (a) and South Louisiana crude oil (b), and relative abundances of C_0–C_{10} alkyl azaarenes in these samples (c and d). Each homologous series is separately normalized and the plots may be compared with PAH plots of Youngblood and Blumer (*20*). Solid circles represent the acridine–benzoquinoline homologue series ($Z = -19$, where Z is defined as $C_nH_{2n+z}N$); crosses the azapyrene–azafluoranthene series ($Z = -21$); open circles the benzacridine–azachrysene series ($Z = -23$)

1,2-benzacridine are comparable in Lake Zurich, while the 3,4 isomer is much more abundant in Lake Lucerne and the street dust than the 1,2 isomer. A similar but more dramatic shift is observed for the dibenzacridines. From such a limited suite of samples, it is of course impossible to determine the environmental significance, if any, of these variations. However, capillary GC offers a technique by which such relative isomer distributions may be investigated.

Analyses of the azaarenes by LVMS provided three significant pieces of information. First, only a small fraction of the total azaarenes isolated from the various samples could be analyzed by GC. This is illustrated by noting that the last compounds eluted by GC are the pentacyclic dibenzacridines (Figure 1), whereas unidentified higher molecular weight components are readily detected by LVMS (Figures 2a and 2b). Secondly, the LVMS results indicate the presence of significant amounts of aza compounds containing two nitrogen atoms (i.e., molecular weights 230, 254, 280, 304, etc., in Figure 2a). This conclusion was supported by GC–MS, but the lack of reference compounds precluded identifications of any of these diazaarenes. Thirdly, information about relative abundances of alkyl homologues of azaarenes was obtained. For example, as was initially indicated by GC, unsubstituted azaarenes predominate over alkyl azaarenes in the surface sediments and street dusts. This observation is shown in the composite mass spectrum of Figure 2a and the corresponding homologue plot in Figure 2c. The addition of each alkyl carbon on the side chain is generally accompanied by a decrease in the relative concentration, and alkyl derivatives containing six or more alkyl carbons were detected. In contrast, the ancient organic matter shows a very different homologue pattern. There is a strong predominance of alkyl derivatives over the unsubstituted parent azaarene, with the highest abundance being for homologues containing four–eight alkyl carbon atoms (Figure 2d).

The molecular distribution of azaarenes in the samples analyzed in this investigation is remarkably like that of PAH in the same samples (*14, 15, 24*). Both compound classes are distributed over similar boiling and molecular weight ranges. In the surface sediments and street dusts, unsubstituted PAH and unsubstituted azaarenes are more abundant than the many alkyl homologues. Similarities between PAH and azaarenes are also seen in the ancient sedimentary organic matter, as represented by the Serpiano oil shale and the two crude oils (*20*). In the case of this fossil material, alkylated PAH and alkylated aza homologues dominate over the unsubstituted parent molecules. However, azaarenes apparently cover a higher boiling range than the PAH in fossil organic material.

Since the aza nitrogen may occupy different ring positions, the azaarene complexity is in fact greater than that of the PAH. Thus, for example, while two unsubstituted three-ringed PAHs (phenanthrene and anthracene) exist, eight three-ringed aza aromatics containing a single nitrogen atom are possible. Indeed, four three-ringed azaarenes are major constituents of the surface sediment and street dust samples analyzed (Figure 1 and Table III). Likewise, four methylphenanthrenes are generally found in environmental samples (*14–16, 24–26*). However, about 14 methylated three-ringed azaarenes were detected by GC–MS. The situation is further

complicated for homologues containing a greater number of alkyl carbons and if two or more nitrogens are present.

Environmental and Geochemical Implications. The presence of an extremely complex mixture of azaarenes in surface lake sediments confirms the earlier finding of these compounds in the Recent sedimentary environment by Blumer et al. (*13*). However, because a wider variety of samples were analyzed in this investigation, the results here suggest that most of the azaarenes in surface sediments have anthropogenic rather than natural origins.

The apparent absence of detectable azaarenes in the deep Lake Lucerne samples leads to two points. First, the conclusion of Blumer et al. (*13*) that azaarenes found in surface marine sediments have resulted from deposition of material produced during natural fires seems unlikely. If natural combustion were an important long-term natural source of aza material, then a relatively constant background of these compounds would be expected to be preserved in aquatic sediments. This assumes a relatively constant level of such fires and a resistance of azaarenes to degradation in the sediments. The older lake sediments should thus contain a complex and measurable azaarene assemblage similar to that of the marine sediments. This is clearly not the case, therefore arguing against natural fires as a significant azaarene source.

Secondly, the older Lake Lucerne sediments contain perylene and a series of phenanthrene homologues that apparently were generated by post-depositional reactions (*16*). However, no azaarenes were detected. This observation suggests that detectable levels of azaarenes are not formed by the same short-term diagenetic processes which can produce PAH. Perhaps azaarenes are indeed generated, but at a level that cannot be detected by this methodology. Lowering the analytical detection limits and/or processing still larger sediment samples might help resolve this question.

The probable origin for the azaarenes in both the Recent marine and lake sediments appears to be anthropogenic. The dramatic difference between azaarene levels in surface sediments of Lake Lucerne and Lake Zurich is attributed to a higher input of anthropogenically derived organic matter in the more heavily populated and industrialized drainage basin of Lake Zurich (*15*). The absence of azaarenes in sediments deposited prior to large-scale anthropogenic activities supports this conclusion. Street dust, similar to that analyzed, may be an important source for the sedimentary azaarenes, as it evidently also is for sedimentary PAH (*15*). Such material may be washed from streets and roads by rainfall, transported by rivers and streams, and eventually accumulated in the sediments. Fallout of atmospheric particulate matter containing azaarenes from fossil fuel combustion is another likely source. The notion of an atmospheric input of anthropogenically generated azaarenes to lake sediments is supported by the results of Dong et al. (*8*) and Cautreels and Van Cauwenberghe (*7*) for analyses of atmospheric particulate material. In atmospheric particulate extracts, azaarenes represent only a few percent of the PAH content, as is the case in the lake sediments. Furthermore, in particulates sampled in a U.S. city (*8*), azaarene concentrations decreased with increasing ring number, while in Europe (*7*), concentrations increased with increasing ring number. This difference was attributed (*7*) to greater coal combustion in Europe compared to the U.S. The azaarene composition of the lake surface sediments is similar to that of the European air particulates, which could suggest that coal combustion is a prime source for the sedimentary azaarenes. Atmospheric fallout will also contribute to the azaarene content of street dust. One fossil fuel combustion product, however, is apparently not an important azaarene source. None of the azaarenes present in the lake sediments and street dusts were found in the automobile engine exhaust analyzed, and the azaarenes that were in the exhaust were not detected in the sediments.

The presence of azaarenes in surface sediments shows that these compounds are cycled through the aquatic environment, with the sediments acting as a sink. Little is known about the long-term biological effects of azaarenes in aquatic systems. Nor is information available dealing with the biogeochemical fate of these compounds. However, one report dealing with bioaccumulation of azaarenes by freshwater zooplankton (*27*) raises the question of possible food chain accumulation in higher organisms, including humans. More data are clearly needed before a better understanding of the sources, effects, and fate of azaarenes in the aquatic environment is achieved. This knowledge is also important considering that production of liquid fuels by gasification of nitrogen-rich oil shale and coal could potentially release increasing amounts of heterocyclic hydrocarbons to the environment in the near future.

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Applicability of Pyrolysis/Gas–Liquid Chromatography for the Identification of Bacteria in Sewage Treatment Plant Effluent

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■ Pyrolysis/gas–liquid chromatography (PGLC) is investigated as a technique to identify bacteria in sewage treatment plant effluent. PGLC shortens the analysis time for bacteria from the 24 to 72 h required by conventional methods to approximately 1 to 2 h. Results indicate PGLC signatures of wet bacterial cells are unique at the species level and can be detected at a lower limit of 50 colony forming units per 100 mL. Analyses of secondary treatment plant effluent have yielded reliable, largely qualitative results in studies conducted to date. Preliminary quantitative data are encouraging but require further development.

As effluent discharge standards become stricter and treatment techniques become more complex, there is a developing need for better process control instrumentation in wastewater treatment plants. Present techniques for determining the bacterial content of water require 24 to 72 h to complete. This long measurement lag creates a potentially unstable operating situation in the control of the process. In addition, conventional measurement techniques are not specific in that they only determine the presence or absence of indicator organisms and, furthermore, are not quantitative. Lastly, pathogenic species of bacteria have recently been detected in samples of drinking water that had few or no indicator organisms detectable by conventional procedures (*1*, *2*).

Pyrolysis/gas–liquid chromatography (PGLC) has been recently employed to determine the composition of bacterial cells (*3*). Pyrolysis breaks down the cells into their biochemical building blocks, whose structure and quantity vary from species to species. Several studies have demonstrated that this technique yields chromatograms that are unique for the species analyzed (*4–6*). The present work is aimed toward developing this technique for the automatic monitoring of bacteria in potable water treatment plant and sewage treatment plant effluents.

Our research centered on identifying samples of wet, filtered cellular material. Samples of pure strains were analyzed to provide a statistically significant reference file of chromatograms. The samples differed in taxonomic classification at the order, family, genus, species, and strain levels. Binary and ternary mixtures of bacteria at various levels of taxonomic diversity were then analyzed by PGLC. A computer program was developed to identify bacteria in samples analyzed by comparing chromatograms of mixtures of species, with chromatograms for the individual strains stored in a computerized reference file (*7*).

Experimental

Apparatus. Pyrolysis of bacterial samples was carried out using a CDS 150 pyrolyzer (Chemical Data Systems, Oxford, Pa.). A probe of platinum wire 152 mm long and 0.36 mm in diameter formed into a coil 3.0 mm i.d. by 15 mm long was used to pyrolyze cells that were loaded into a 3.0 mm o.d. quartz sample tube as depicted in Figure 1. With the tube in place, the probe was inserted into a heated interface attached to the inlet of gas chromatograph. Figure 2 is an exploded view of the pyrolysis probe, quartz sample tube, and gas chromatograph interface.

All chromatographic analyses were carried out on a Varian Model 2700 dual column gas chromatograph (Varian Instrument Division, Palo Alto, Calif.). The pyrolysate was eluted onto a column packed with 110–120 mesh Chromosorb W, washed with acid and treated with dimethylchlorosilane. The column was coated (5% by weight) with Carbowax 20M-TPA. During operation, the columns were programmed from 30 °C at ignition of the probe to 250 °C at the rate of 10 °C/min. The columns were then held at 250 °C until the analysis was complete, approximately 45 min after ignition of the pyrolyzer. These do represent relatively severe operating conditions for these columns, which resulted in a usable column life of approximately 1100 analysis cycles. Columns were replaced when the loss of support phase resulted in poor separation as identified by the loss of total peak response and/or the loss of peaks from the final minutes of the chromatogram. The dual hydrogen flame ionization detectors were maintained at 275 °C

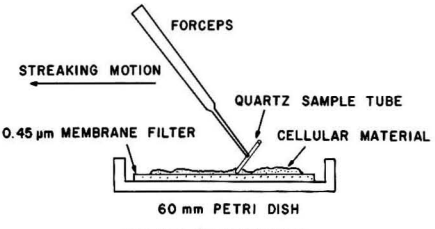

Figure 1. Sample loading

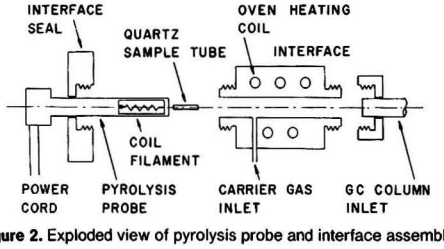

Figure 2. Exploded view of pyrolysis probe and interface assembly

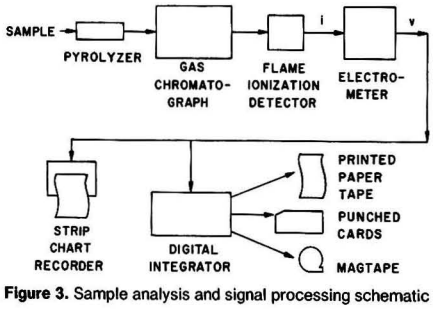

Figure 3. Sample analysis and signal processing schematic

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Table I. Taxonomic Classification of Bacteria

order	family	genus	species	ATCC strain no.
Eubacteriales	Micrococcaceae	*Streptococcus*	*faecalis*	19433
	Enterobacteriacae	*Escherichia*	*aurescens*	12814
			coli	11303*
				12435
		Enterobacter	*aerogenes*	13048
		Proteus	*rettgeri*	25932
		Salmonella	*typhimurium*	23564
		Shigella	*flexneri*	12661
			sonnei	9290
Pseudomonadales	Pseudomonadaceae	*Pseudomonas*	*aeruginosa*	10145
			fluorescens	13525

Table II. Mean Retention Times and Peak Area Percents for *E. coli* ATCC 11303 (*N* = 46 Samples)

peak no.	mean retention time, min	std dev, min	mean peak area, %	std dev, %	peak no.	mean retention time, min	std dev, min	mean peak area, %	std dev, %
*	0.37	0.06	0.0407	0.0120	22	13.61	0.04	1.2526	0.2634
1	0.50	0.01	42.6616	1.5239	23	14.22	0.05	0.2919	0.0238
2	0.77	0.02	0.0792	0.0216	24	14.83	0.05	1.1767	0.2398
*	0.81	0.08	0.7131	0.0533	25	15.28	0.05	0.1553	0.0066
*	0.93	0.06	0.3079	0.0010	26	16.21	0.05	0.5855	0.0652
3	1.10	0.03	0.0606	0.0454	27	16.78	0.05	0.4117	0.0387
4	1.25	0.04	0.0603	0.0220	28	17.19	0.05	3.4627	0.0367
*	1.39	0.12	0.2168	0.0346	29	17.90	0.04	0.8007	0.0272
*	1.61	0.06	0.7935	0.0350	30	18.41	0.04	0.4687	0.1626
5	1.78	0.02	3.2963	0.5166	31	18.80	0.05	2.6359	0.5515
*	1.89	0.06	0.8485	0.0222	32	19.64	0.04	0.3868	0.0997
*	1.98	0.06	1.4577	0.1600	33	19.88	0.04	0.5251	0.0784
*	2.06	0.11	0.9906	0.1430	34	20.25	0.04	0.3011	0.0019
*	2.34	0.09	0.8284	0.1054	35	21.01	0.05	1.7811	0.5092
6	2.53	0.03	1.6048	0.3200	36	21.27	0.05	0.4373	0.0894
7	2.76	0.02	3.7560	0.8139	37	22.63	0.04	1.1474	0.5550
*	3.24	0.07	0.8636	0.0954	38	23.06	0.02	2.6536	0.1265
*	3.39	0.09	0.4041	0.1006	39	23.42	0.05	0.6809	0.0842
8	4.01	0.02	0.1781	0.0145	40	24.15	0.03	1.2326	0.0579
9	4.48	0.02	0.4380	0.0654	41	24.75	0.03	0.2749	0.0080
10	4.81	0.04	0.0563	0.0059	42	25.02	0.02	0.8286	0.1052
11	6.30	0.03	0.4870	0.0872	43	25.39	0.05	1.0761	0.6337
12	6.80	0.04	0.2562	0.0246	44	26.73	0.03	0.6857	0.0789
13	7.22	0.04	0.9470	0.0437	45	27.81	0.03	2.7898	0.2992
14	7.87	0.04	0.1262	0.0990	46	29.16	0.02	1.0919	0.5120
15	8.62	0.03	0.2879	0.0801	47	30.49	0.05	1.1983	0.8943
16	9.18	0.05	0.4474	0.0625	48	31.27	0.05	0.7035	0.0945
17	10.35	0.02	0.1627	0.0196	49	32.28	0.04	1.3188	0.8594
18	11.52	0.05	0.6683	0.0125	50	33.18	0.04	1.0021	0.2796
19	12.12	0.03	0.2334	0.0642	51	34.38	0.05	1.6408	0.3654
20	12.41	0.05	0.1847	0.1220	52	36.46	0.03	2.0252	0.0762
21	12.96	0.03	1.2086	0.0987	53	41.50	0.04	0.1439	0.0054
								99.83	

under hydrogen flowing at 0.5 mL/s and air zero gas at 5 mL/s. The detector electrometer was operated at a sensitivity of 2 $\times 10^{-10}$ A/mV.

The chromatograph was fitted with Varian dual hydrogen flame ionization detectors, whose current output was converted to a potential signal by a Varian dual-differential electrometer. The electrometer output was recorded on a strip chart recorder. The electrometer output was also digitized by a Varian Model 101 electronic digital integrator whose printed output included the peak number, method of separation of adjacent peaks, retention time, peak area, and peak area percent. The output of the integrator is in two forms, digital d.c. electronic voltage pulses and hard copy digital paper tape. While the electronic signal could be recorded on magnetic tape or interfaced directly with a computer, we chose the less expensive option of punching cards from the paper tape readout. A block diagram of the sample analysis and signal processing equipment is depicted in Figure 3.

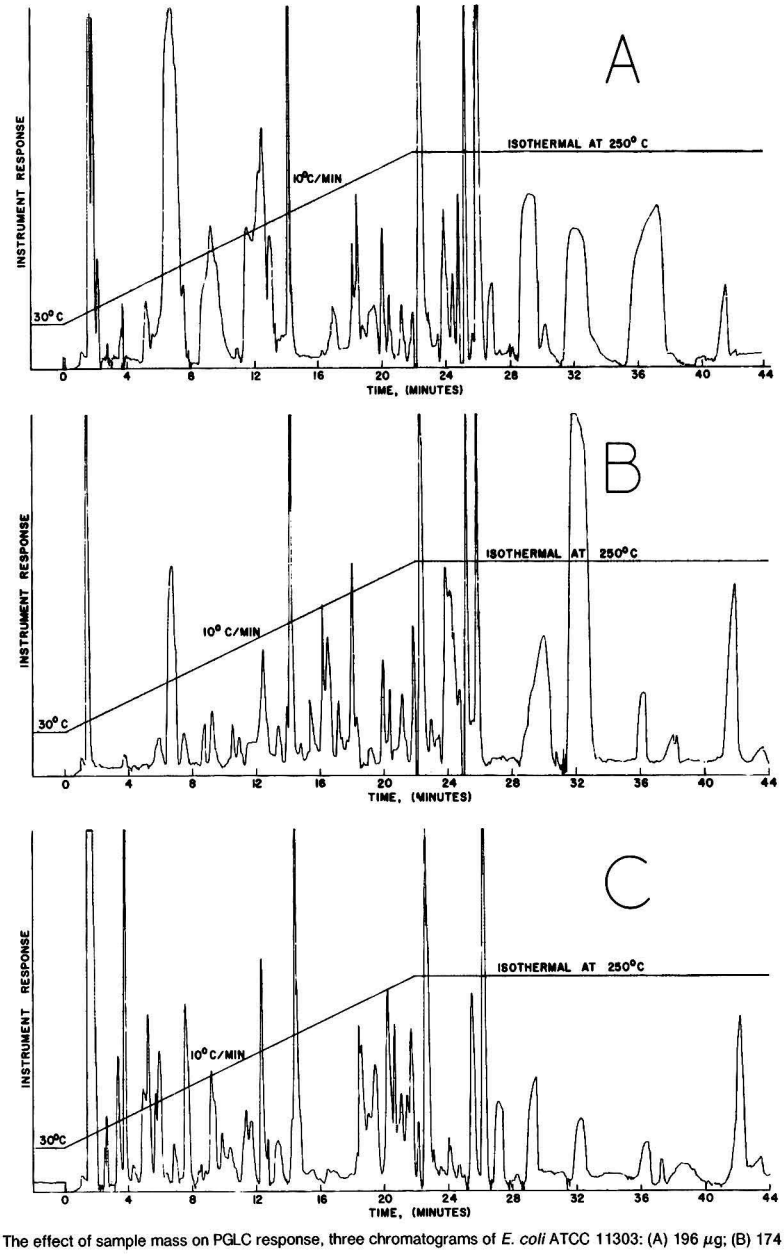

Figure 4. The effect of sample mass on PGLC response, three chromatograms of *E. coli* ATCC 11303: (A) 196 μg; (B) 174 μg; (C) 52 μg

Stock Cultures. In order to have reference strains of bacteria differing at the order, family, genus, species, and strain levels, 11 different cultures were used in the study. These were obtained in lyophilized (freeze-dried) form from the American Type Culture Collection (ATCC), Rockville, Md. The taxonomic classification of the bacteria used is reported in Table I.

Procedure. Cells from the stock cultures were prepared for PGLC analysis by vacuum filtering 20-mL portions of refrigerated (2 °C) culture material through a 0.45-μm membrane filter. The filters were then washed with 100 mL of sterile water and placed in 60-mm sterile petri dishes for storage prior to sampling.

Samples to be pyrolyzed were loaded into preweighed, sterile quartz sample tubes by moving an open end of the tube over the cell mass on the filters as depicted in Figure 1. The loaded tubes were then weighed on a Cahn RG electrobalance. Immediately after weighing, the loaded sample tubes were placed in the coil probe. The probe was then inserted into the pyrolysis interface which was maintained at 175 °C under a

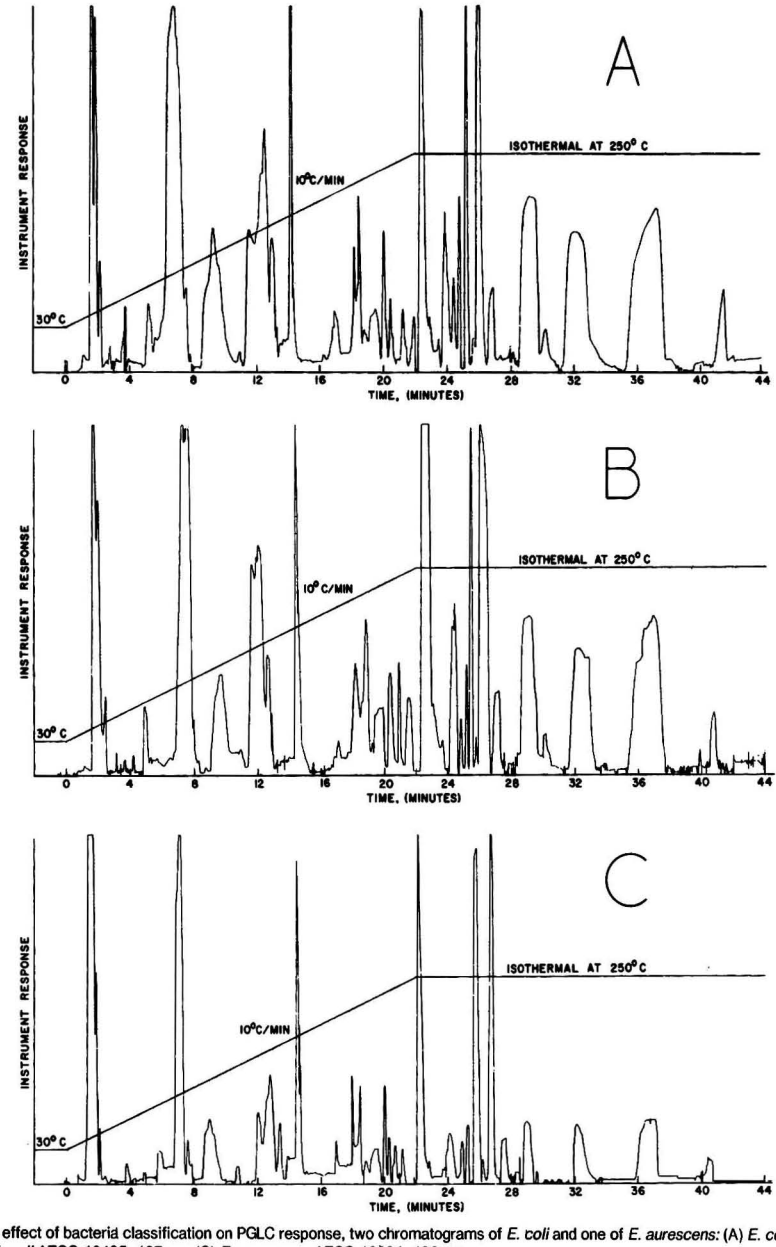

Figure 5. The effect of bacteria classification on PGLC response, two chromatograms of *E. coli* and one of *E. aurescens:* (A) *E. coli* ATCC 11303, 196 μg; (B) *E. coli* ATCC 12435, 187 μg; (C) *E. aurescens* ATCC 12804, 192 μg

helium carrier gas stream at a flow rate of 0.5 mL/s.

Two minutes was required for the interface and chromatograph to reach equilibrium, as detected by stable recorder base line, after which the sample was pyrolyzed at 900 °C for 10 s. The pyrolysis products were swept into the gas chromatographic column and analyzed as described. Data were recorded by the digital integrator that was started simultaneously with the ignition of the probe and was terminated automatically at the end of the analysis cycle (~0.75 h).

Experiments were also conducted with two or more species of bacteria. The procedure for these experiments was the same as for those involving a single bacterium, except the 20-mL portions of culture material consisted of smaller aliquots of culture material from each individual stock culture.

Duplicate samples of cells were analyzed according to prescribed (*8*) membrane filter procedures by taking cellular material from the filters with a quartz sample tube, weighing the material, and resuspending it in 100 mL of sterile water. This sample was serially diluted to 1/10, 1/100, and 1/1000 the initial concentration. The four resulting samples each were vacuum filtered through a 0.45-μm membrane filter and washed with 50 mL of sterile water. The filters were then in-

cubated according to the membrane filter technique recommended for the species being analyzed. After incubation, the colonies were counted under a microscope at 20× and recorded as colony forming units (CFU's) per 100 mL.

Results and Discussion

We identified mixtures of bacteria by using a computer program to compare peak retention times of the sample chromatogram to those in a reference file. If a match was found, the program would subtract that reference chromatogram of the sample and then search for additional matches.

This process required two preliminary sets of experiments. First, a reference file was built using the different bacteria of interest. This was done by performing a statistically significant number (at least 30) of PGLC runs and averaging the retention times and peak areas for all peaks for each bacterium. After the reference file was completed, it was stored on magnetic tape. If the standard deviation for each of these two measurements is small, then a simple matching and subtraction technique should readily be able to differentiate between bacterial profiles stored in the reference file.

In addition, we compared the sum of the peak areas with the amount of sample pyrolyzed. A strong correlation between these two quantities could lead to a determination of the relative amounts of bacteria in mixtures if the correlation is independent of the species of bacteria.

To illustrate the repeatability of the PGLC method, we present here, as Figure 4, 3 of the 46 chromatograms which were made to generate the data file on *Escherichia coli*, American Type Culture Collection (ATCC) 11303. Figures 4A and 4B were chosen as representative of samples of about the same weight (196 and 174 μg), while Figure 4C is the chromatogram of a sample considerably lower in weight (52 μg). Note that the upper two chromatograms are virtually identical. The lower one has smaller peaks but these occur at essentially the same times. Some of the individual peaks are not reproducible, for example, the peaks at 4.9 and 27.4 min. When the entire 46 runs were analyzed, 11 peaks had standard deviations of peak area and/or retention times which were greater than our tolerance limits (±5% for peak area and 0.05 min for retention time). These limits were established on a trial and error basis by using the computer program to identify samples of known species of bacteria with data stored in the reference file. Table II is the summary of this data. In accordance with our tolerance limits, the 11 peaks marked with asterisks were deleted from the computerized data file. This permitted consistent, reliable computer matches to be obtained between the reference file and samples of known bacterial composition. While the 11 peaks represent approximately 15% of the number of events in the chromatogram, their elimination from the reference file is not significant. These peaks, and most others discarded in the generation of reference chromatograms for the other species, occur in the first 10 min of the chromatogram where there are many peaks. Since many sequential peaks in this portion of the chromatogram are skewed and have peak widths up to 0.1 min in duration, precise matching of peaks in this region is extremely difficult. This problem does not occur in analyzing the last 30 to 35 min of the chromatogram where the number of peaks are fewer and more widely spaced and the chromatograms are more unique from one species to the next.

At least 48 and as many as 60 reproducible peaks were detected in each of 11 strains of bacteria we studied. This compares favorably with the 30 to 40 peaks reported by Reiner (*9*). The slightly larger number of peaks in the present work may be due in part to the higher pyrolysis temperature used, 900 vs. 800 °C. Our attempts at even higher temperatures produced fewer peaks, all of which eluted faster. It appears the pyrolysis products at higher temperatures are a small number

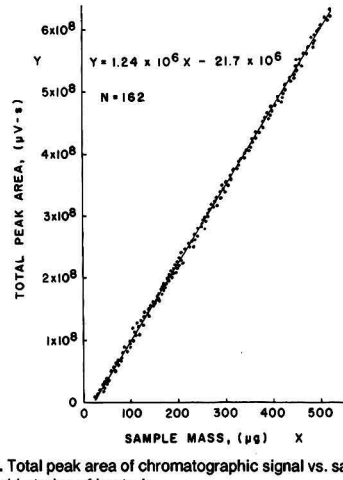

Figure 6. Total peak area of chromatographic signal vs. sample mass (wet) for 11 strains of bacteria

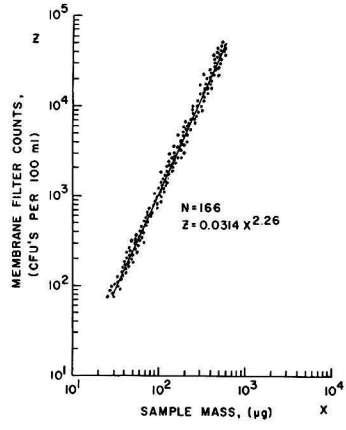

Figure 7. Membrane filter counts vs. sample mass (wet) for 11 strains of bacteria

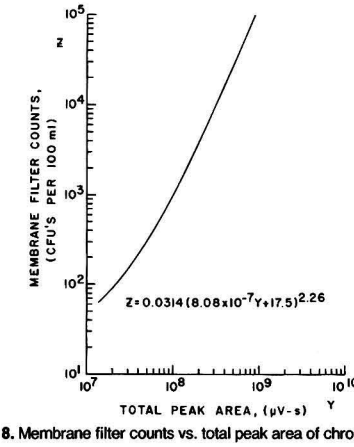

Figure 8. Membrane filter counts vs. total peak area of chromatographic signal

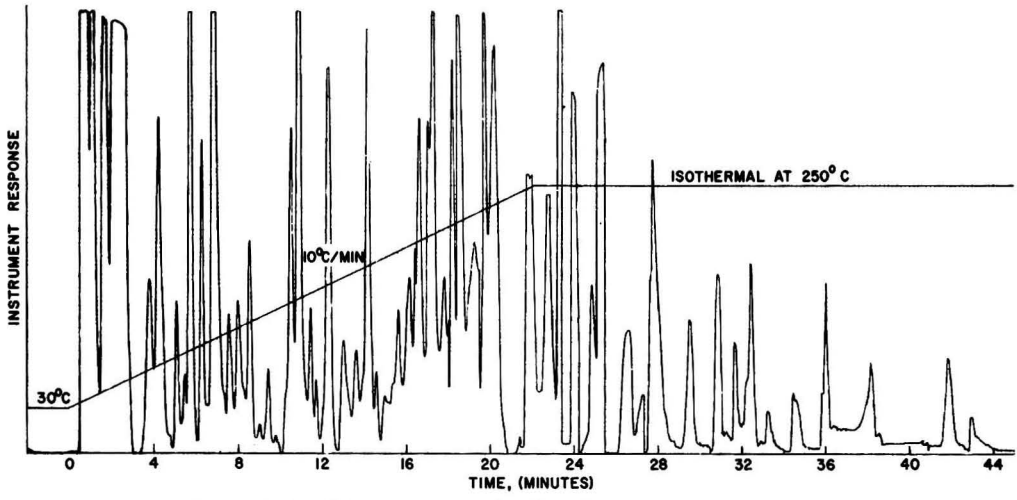

Figure 9. Composite *E. coli* chromatogram, approximately equal amounts of ATCC 11303 and ATCC 12435

of compounds that differ only slightly from one species to another.

The variation in the chromatograms of the different bacteria is illustrated in Figure 5, which represents two strains of one species, and two species from the same genus. Figures 5A and 5B represent two strains of the same species (*E. coli*, ATCC 11303 and ATCC 12435, respectively). Figures 5B and 5C represent two species of the same genus (*E. coli* ATCC 12435 and *E. aurescens* ATCC 12814, respectively). The three chromatograms have been chosen such that the sample weights are about the same. We note there is less variation in retention times and peak areas between the two strains of *E. coli* than there is between either of the two *E. coli* strains and *E. aurescens*. We concluded that the method, as we have applied it, is sensitive enough to differentiate between two taxonomically related species of bacteria, but perhaps not between two strains of the same bacterium.

Since there is some visual difference between the chromatograms of the two *E. coli* strains, we analyzed them in detail to see if the difference is great enough to differentiate between them. To do this we matched the signature information of the two strains in turn with the statistical information stored for all bacteria on magnetic tape. We found we could identify the chromatogram of individual bacterial species. However, the computer match could not discriminate between the two strains if the species was *E. coli*. At this time, we do not know if the limitations to reliable identification and differentiation at the strain level are due to inherent limitations in the equipment, the analytical procedure, or our identification algorithm.

In addition to the qualitative results already described, we used the computer program to obtain quantitative results from the PGLC analyses of individual strains and mixtures of strains. By recording the total peak area response obtained from the PGLC analyses of preweighed samples of cellular material, we were able to obtain the signal response to cellular mass relationship depicted in Figure 6. As can be seen from the graph, the signal response was fairly linear for samples having masses between 50 and 500 μg. In order to permit a direct comparison between the number of CFU's detected by membrane filter counts and PGLC response, duplicate samples of weighed cellular material were incubated for subsequent colony counting. As can be seen from Figure 7, an exponential relationship between membrane filter counts and sample mass was found. By equating the two expressions obtained in terms of the mass of cellular material, the equation and graph on Figure 8 resulted. This equation:

$$Z = 0.0314(8.08 \times 10^{-7}Y + 17.5)^{2.26} \quad (1)$$

where Z = membrane filter counts, CFU's per 100 mL, and Y = total peak area, μV·s, was used in analyzing mixtures of bacteria to determine the contribution to the chromatogram due to each individual species present in the sample.

When the computer program finds all the peaks in one of the reference files are present in a sample, it subtracts the scaled mean peak areas of that reference file from the sample chromatogram. The scale factor is computed so as to subtract the most signal without any residual peak area being negative. It is then used to quantify the amount of that bacteria present in the sample by using Equation 1. Results from the analysis of mixtures of stock cultures indicate the procedure is highly reliable in the identification of these samples.

To see what this technique would yield when applied to a mixture of two strains of the same bacteria, a sample was prepared containing approximately equal amounts of the two *E. coli* strains. Figure 9 is a chromatogram of this mixture. As can be seen by comparing Figure 9 with the representative *E. coli* chromatograms in Figures 4 and 5, it is visually difficult to identify those peaks attributable to each strain. This was verified by using the computer program, which was not able to recognize that two strains were present. From an environmental standpoint, this result is a desirable one. A method so sensitive as to differentiate at the strain level would probably not be useful in the analysis of secondary treatment plant effluent.

Work has begun on the detailed analysis of environmental samples. We are attempting to improve results at the strain level of diversity and to determine whether the procedure can be used to differentiate between whole, viable cells and dead cellular material. Refinements and adjustments must be made, primarily in the areas of sample preparation and the computer matching procedure. Preliminary results, though, show that with further modification the method can be applied for the analysis of bacteria in samples of sewage treatment plant effluent.

Conclusions

- PGLC analysis of species of bacteria yielded chromato-

grams unique for each species analyzed.

- A computer program was written that permitted the identification of individual species in mixtures of stock cultures.
- The PGLC technique/computer program was not able to differentiate between different strains of the same species of bacteria.
- Relationships were obtained between signal response, colony counts, and the mass of cells analyzed. The relationships were capable of quantitatively differentiating between different species in mixtures of stock cultures.
- The PGLC procedure/computer program could be used to a limited extent in identifying bacteria in samples of secondary treatment plant effluent.

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Silicon and Aluminum in Urban Aerosols for Characterization of Atmospheric Soil Particles in the Nagoya Area

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■ Measurements of size distributions and concentrations of Si and Al in urban aerosols were made in Nagoya, Japan, and the behavior of the atmospheric soil particles is described. The size distributions for both elements suggest that more than 90% of the mass of Si and Al in the atmosphere originates from soils. The average concentrations of Si and Al in the three seasons except spring were 2.30 and 0.812 $\mu g/m^3$, respectively. In the spring, yellow sand dusts called Kōsa were transported from North China to Japan, so that the concentrations of both elements increased to 5.33 and 1.88 $\mu g/m^3$, respectively. However, the size distributions and the concentration ratio of Si/Al were almost constant throughout the year. The contribution of soil dust to the total suspended particulate matter is also discussed.

Measurements of the size distributions and chemical compositions of particles in ambient air are important in understanding the sources, behavior, and mechanisms of formation of particles in the atmosphere.

It is generally concluded that fine particle sizes arise from man's activities, including combustion processes and the conversion of pollutant gases, whereas coarse particle sizes originate mainly from natural activities, such as wind erosion of land and sea surfaces (*1, 2*). Whitby and co-workers (*3–6*) have reported that the size distribution of atmospheric particles is usually bimodal, with one mode occurring below 1–2 μm and another in the 5–15-μm range. In the previous papers of this series (*7, 8*), the author represented the relationship between the bimodal distribution of atmospheric particles and the size distributions of sulfate, nitrate, and ammonium, which were principal components associated with secondary particles from anthropogenic sources. Atmospheric soil particles comprise the bulk of primary particles from natural sources as well as sea salt particles. Si and Al are the two most abundant elements in the crust next to oxygen, so that the size distributions for Si and Al in atmospheric particles contribute to an understanding of the behavior of soil particles in ambient air. On the other hand, the concentration ratio of Si/Al in atmospheric particles is also important in estimating the mineral composition of soil particles (*9*). The size distribution for Al has been reported by several groups of workers (*10–13*); however, the information on the size distribution for Si is very meager because of the difficulties in fractionating and collecting sufficient materials for chemical analysis. The present study was undertaken to clarify the size distributions for Si and Al in atmospheric particles and the relationship between the size distribution of total suspended particulate (TSP) and those of both elements. Measurements were made in Nagoya from September 1976 to September 1978. Fractions of particles collected with an Andersen cascade impactor were analyzed for Si and Al by means of spectrophotometric methods after alkaline fusion. From the results of the size distributions and concentrations for Si and Al, the behavior of atmospheric soil particles in the Nagoya area could be discussed.

Experimental

Sampling Procedure. Air samples were collected at the Aichi Environmental Research Center in a mixed residental/light industry area of Nagoya by use of a Model 21-000 Andersen sampler manufactured by 2000 Inc. The sampler consisted of eight stages followed by a Whatman 41 (cellulose) backup filter. Atmospheric particles were fractionated into size classes <0.43, 0.43–0.65, 0.65–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–7.0, 7.0–11, and >11 μm equivalent aerodynamic diameter.

The sampler was operated at 1 cfm (28.3 L/min); the collecting surfaces were stainless steel plates. In order to collect enough particles for chemical analysis, sampling times were 5–8 days, depending on air pollution and weather conditions.

Analysis of Silicon and Aluminum. Atmospheric particles collected on each impactor plate were scraped with a "policeman" and transferred respectively to 200-cm^3 beakers with

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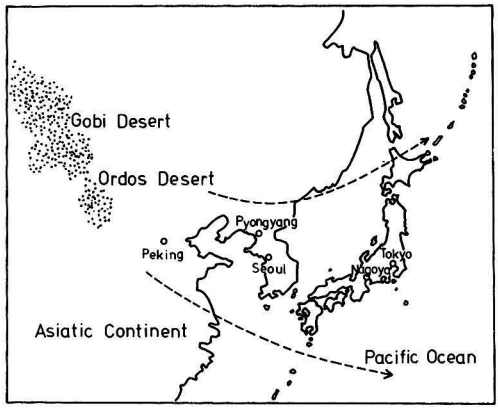

Figure 1. Approximate trajectory of yellow soil dust called Kōsa from North China to Japan

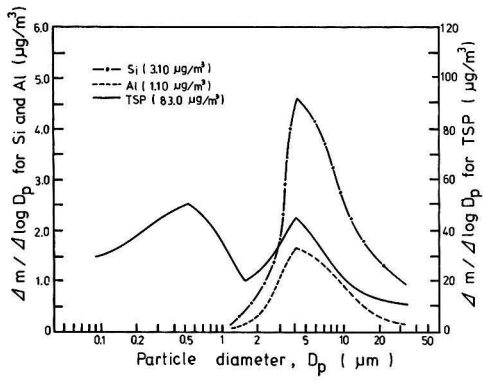

Figure 3. Size distributions for silicon, aluminum, and TSP at Nagoya, May 12–18, 1978

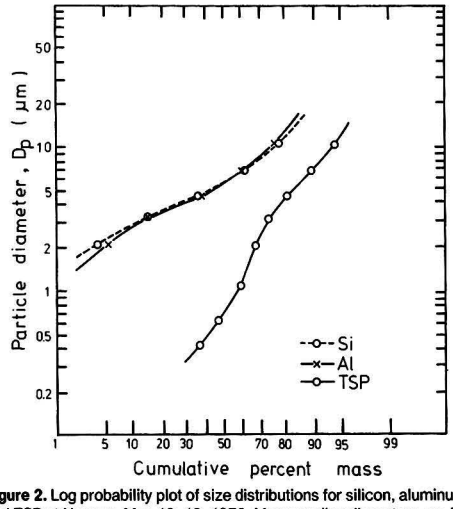

Figure 2. Log probability plot of size distributions for silicon, aluminum, and TSP at Nagoya, May 12–18, 1978. Mass median diameters are 5.7 μm (Si), 5.8 μm (Al), and 0.68 μm (TSP)

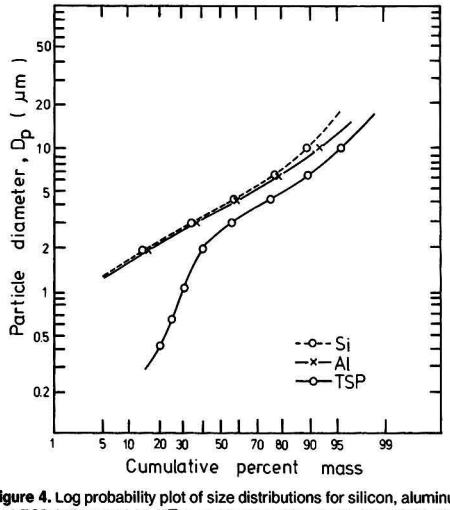

Figure 4. Log probability plot of size distributions for silicon, aluminum, and TSP influenced by Kōsa at Nagoya, March 12–18, 1977. Mass median diameters are 4.2 μm (Si), 4.0 μm (Al), and 2.9 μm (TSP)

150 cm^3 of distilled water. The suspended solutions were filtered by use of Toyo No. 7 (cellulose, 11 cm diameter) filters.

The water-insoluble fractions collected on the filters were dried by keeping them in a drying oven for 1 h at 100 °C and ashed in 30-cm^3 nickel crucibles at 550 °C, and then solubilized by fusion with Na_2CO_3 (300 mg) over a Meker burner. The fused samples were dissolved with water and analyzed for Si and Al by absorption spectrophotometry. The backup filter was ashed in a nickel crucible at 550 °C and treated in the same way as the impactor plates. Si was determined by the molybdenum blue method (*14, 15*) for which a coefficient of variation, CV, of 8% was found. Al analysis was done by the Chromazurol S–hexadecyltrimethylammonium chloride method (*16*). The CV of this method was about 10%. The accuracy of the procedure, established by ashing, fusion, and analysis of the cellulose filters spiked with known amounts of Si and Al, averaged 95% (*17*).

Size distribution curves of TSP, Si, and Al were calculated as in the previous papers (*7, 8, 18*), but in this paper the particle size range, $\Delta \log D_P$, was used instead of $\Delta \ln D_P$, following Husar's advice (*19*).

Results and Discussion

When atmospheric soil particles in Japan are discussed, the influence of the yellow loess particles called "Kōsa" must be taken into consideration. In the arid desert regions of North China and Mongolia of the Asiatic Continent, heavy dust storms frequently occur on a very wide scale in the spring. Kōsa is the yellow sand dust that arises from a dust storm in an arid area of the northern part of China, which is transported to Japan (Figure 1). These yellow soil particles are observed in almost all regions of Japan, especially in spring.

Figure 2 shows typical examples of cumulative size distribution of Si, Al, and TSP in urban air at Nagoya, and those size distribution curves are shown in Figure 3. As shown in Figure 2, about 95% of the atmospheric Si and Al were concentrated in the particles larger than 2 μm in diameter. Most of the mass of Si and Al was found in the particle size range of 3–7 μm diameter. The mass median diameters (mmd's) of Si and Al were 5.7 and 5.8 μm, respectively. The shape of the Si cumulative size distribution curve was in good agreement with that of Al, and the log probability plots gave an ap-

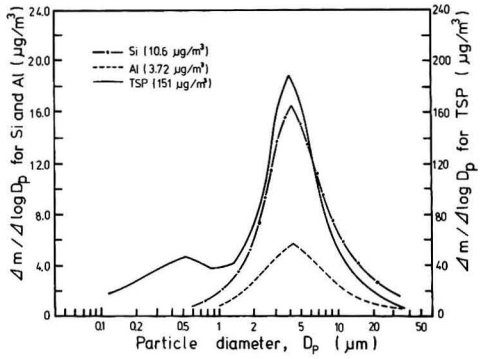

Figure 5. Size distributions for silicon, aluminum, and TSP influenced by Kōsa at Nagoya, March 12–18, 1977

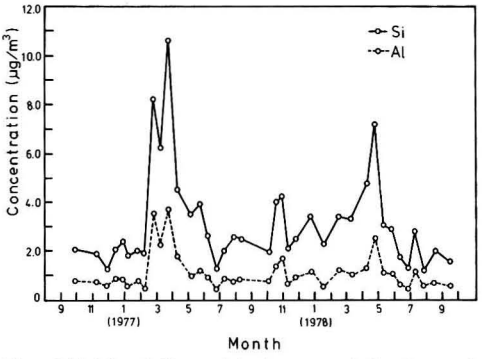

Figure 6. Variation of silicon and aluminum concentrations in aerosols at Nagoya, September 1976–September 1978

Table I. Size Characterization of Atmospheric Silicon and Aluminum at Nagoya (September 1976–September 1978)

sampling period	no. of samples	av mmd, μm		av % of mass > 2.1 μm in diam	
		Si	Al	Si	Al
spring (Mar–May)	10	5.7	5.1	93	93
summer (June–Aug)	10	6.6	6.0	93	92
autumn (Sept–Nov)	9	5.6	5.1	91	92
winter (Dec–Feb)	9	6.4	5.6	90	91

Table II. Average Concentrations of Atmospheric Silicon, Aluminum, and TSP at Nagoya (September 1976–September 1978)

sampling period	no. of samples	Si, μg/m³	Al, μg/m³	concn ratio of Si/Al	TSP, μg/m³
spring	10	5.33	1.88	2.8	86.9
summer	10	2.05	0.747	2.7	76.7
autumn	9	2.43	0.901	2.7	71.5
winter	9	2.42	0.788	3.1	57.8

proximately straight line. The size distribution of TSP was a bimodal distribution consisting of a coarse (>2 μm diameter) and fine (<2 μm diameter) particle peak, as seen in Figure 3. In contrast to TSP, the size distributions for Si and Al were approximately log normal, and both were in good agreement with the coarse particle peak of TSP.

Figure 4 shows the cumulative size distributions of Si, Al, and TSP in urban air at Nagoya when Kōsa was observed clearly, and those size distribution curves are shown in Figure 5. The size distribution of TSP influenced by Kōsa changed remarkably in comparison with that of TSP in the usual urban air, as shown in Figure 3, i.e., the distribution shifted toward large particle size and the coarse particle peak was predominant. On the other hand, in spite of a marked increase of the concentrations, the size distribution patterns for Si and Al did not change, except the mmd's of Si and Al became only slightly smaller.

The mmd's of Si and Al on March 12–18, 1977, were 4.2 and 4.0 μm, respectively. This slight shift of Si and Al mmd's toward a smaller size suggests that the large soil components of Kōsa (e.g., quartz) fall out as Kōsa is transported to Japan over the sea, in contrast to the small soil components (e.g., clay minerals) that remain in the atmosphere. In Figure 5 the shapes of the Si and Al size distribution curves were almost completely log normal. Table I summarizes the average mmd's

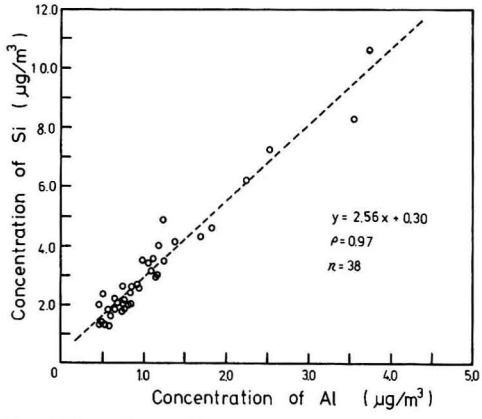

Figure 7. Scatter diagram of silicon and aluminum in aerosols at Nagoya, September 1976–September 1978

and percent mass > 2.1 μm in diameter of Si and Al for the four seasons at Nagoya from September 1976 to September 1978. The size distribution patterns of atmospheric Si and Al described above were constant throughout the year. More than 90% of the mass of Si and Al was found in particles larger than 2 μm in diameter.

Figure 6 shows the variation of concentrations of Si and Al in urban air at Nagoya. The concentrations of Si and Al changed periodically with the season. The high concentrations were found in the spring. The maximum concentrations of Si and Al were 10.6 and 3.72 μg/m³; on the other hand, the minimum concentrations were 1.23 and 0.436 μg/m³, respectively.

Table II lists the average concentrations and concentration ratios of Si and Al for the four seasons at Nagoya. The average concentrations of Si (5.33 μg/m³) and Al (1.88 μg/m³) in the spring were about 2.3 times higher than those in the other three seasons (Si = 2.30 μg/m³, Al = 0.812 μg/m³). It is indisputable that the high concentrations of both elements in the spring are due to the influence of Kōsa. However, the concentration ratio of Si/Al did not change throughout the year, in no connection with the influence of Kōsa.

The overall arithmetic mean Si/Al (N = 38) was 2.9, with a standard deviation of only 0.24 and a CV of 8.3%. Figure 7 is a scatter plot for the concentration of Si against that of Al. The correlation coefficient for these data is 0.97. The atmospheric Si/Al ratio is very significant to estimate the mineral

Table III. Concentrations of Aluminum in Soils

soils	concn of Al, %	
	Al_2O_3	Al[a]
alluvial soil[b]	12.39	6.6
in Japan	10.79	5.7
brown forest soil[c]	18.5	9.8
in Japan		
loess in China[d]	11.94	6.3
	9.56	5.1
	15.44	8.2

[a] Al percent values are calculated from the data of Al_2O_3 percent. [b] From ref 24. [c] From ref 25. [d] From ref 26.

Table IV. Contribution of Soil Particles to TSP Matter at Nagoya

sampling period	no. of samples	obsd concn of Al, $\mu g/m^3$	predicted[a] concn of soil particles, $\mu g/m^3$	contribution of soil particles to TSP matter, %
spring	10	1.88	31.3	36.0
summer	10	0.747	12.5	16.3
autumn	9	0.901	15.0	21.0
winter	9	0.788	13.1	22.7

[a] Values are calculated by use of Al concentration in soils of 6%.

composition of the atmospheric soil particles. This remarkable Si–Al correlation and the size distributions for Si and Al described above suggest that not only do the atmospheric Si and Al originate almost entirely from the soil, but, also, the soil components of the atmospheric soil particles do not change very much. From the results of Figures 2–5 and 7 and Table II, it is appropriate to consider that the contribution of atmospheric soil particles to TSP matter can be obtained by using the two Al (or Si) concentrations in the atmosphere and soil. The Al concentration is usually used to estimate this contribution.

Bear has reported that the Al content of soils, expressed on the basis of Al_2O_3, frequently is in the range of 2–12% (*20*). Miller et al. (*21*) have reported the Al concentration in soil dust of 8.2%, and Friedlander (*22*) has estimated that the contribution of soil dust to TSP matter is 11.4% in Pasadena. On the other hand, Kowalczyk et al. (*23*) have used the Al concentration in soils of 5.6% to estimate this contribution in the Washington area, and estimated that the concentration of atmospheric soil particles is 21.4 $\mu g/m^3$.

In Table III are summarized the Al concentrations of the soils that are most abundant on the land surfaces of Japan (*24, 25*) and the Al concentrations of loess in China (*26*), which is the source of Kōsa.

In the present study, the contribution of atmospheric soil particles to TSP matter has been calculated, assuming that the Al concentration in soils is about 6%. The predicted concentration and contribution of atmospheric soil particles are summarized in Table IV. The average predicted concentration of atmospheric soil particles in the three seasons except spring was about 14 $\mu g/m^3$, and the contribution of about 20% to TSP matter was estimated. In the spring period influenced by Kōsa, a twofold increase of these was found in comparison with the other seasons.

Summary

The size distributions and concentrations of Si and Al in urban aerosols at Nagoya were measured for the characterization of atmospheric soil particles. The Si and Al were predominantly associated with coarse particles. The size distributions and concentrations of both elements suggest that more than 90% of the mass of Si and Al in the atmosphere originates from soils. It was estimated that the background concentration of soil dust was about 14 $\mu g/m^3$, and the contribution of soil dust to TSP matter was about 20%. However, in the present study the errors of bounce-off and wall loss in the sampling procedure are not taken into consideration, so that the concentrations and mmd's of Si and Al may be somewhat increased compared to those presented above.

Acknowledgment

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Trihalomethane Yields as a Function of Precursor Molecular Weight

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■ The trihalomethane (THM) yield on a total organic carbon (TOC) basis was measured as a function of the molecular weight of precursor organics in the Iowa River. Gel permeation chromatography with Sephadex G-75 gel was utilized to separate naturally occurring organics into apparent molecular weight fractions that were subsequently chlorinated to 2 mg/L of free residual and analyzed for THMs. Ninety percent of the organics in the Iowa River were of mol wt less than 3000, while 75% of the THMs were derived from the mol wt less than 3000 fraction. It was found that bromoform was derived from only the smallest organics of mol wt less than 1700.

The National Organics Reconnaissance Survey (NORS) was sponsored by the U.S. Environmental Protection Agency (EPA) in 1974 and 1975 to determine the concentrations of carbon tetrachloride, 1,2-dichloroethane, and four trihalomethanes (THMs), which were chloroform, bromodichloromethane, dibromochloromethane, and bromoform in 80 city water supplies (*1*). Contamination of drinking waters with these known or suspected carcinogens was widespread at the parts per billion level. About the same time, Rook (*2*) and Bellar et al. (*3*) stated that halogenated organics are formed during the chlorination of water for disinfection. Subsequently, the National Organics Monitoring Survey (NOMS) was conducted to determine the frequency and concentration of many specific organics in drinking water supplies (*4*). The result of these surveys and the Safe Drinking Water Act of 1974 (PL 93-523) has been the proposal of a maximum contaminant level (MCL) of 100 μg/L for trihalomethanes published by the U.S. EPA in the *Federal Register* on Feb 9, 1978.

The formation of THMs in water treatment plants during and following chlorination involves the reaction between hypochlorous acid and organics to form chlorinated organics including THMs. The chemical nature of the organic precursors and the reaction mechanisms have been hypothesized (*5–8*), but experimental data on the molecular weights (mol wt) of these precursors are lacking.

Because control of THM production by precursor removal may be the best approach for decreasing THMs in finished water, knowledge of the precursor identity and molecular weight is valuable. This information may be useful in the design of adsorbents or other treatment systems and provide clues as to the origin of these compounds. The objective of this study was to determine the apparent molecular weight range of THM precursor compounds in the Iowa River and Coralville Reservoir near Iowa City. Soluble organics from Iowa River water were size-fractionated by gel permeation chromatography, and the fractions were chlorinated and analyzed for THM yields by electron-capture gas chromatography.

Site Description

Samples for this investigation were obtained above and below the Coralville Reservoir. Upstream samples were collected at Johnson County Road 0. Samples at the outflow for the reservoir were collected from the Iowa River about 1 mile below the Coralville Dam, at old highway 218.

The Iowa River Basin is located in the eastern half of Iowa. The river rises in north-central Iowa and flows in a southeasterly direction for approximately 255 miles before entering the Coralville Reservoir. The drainage basin comprises an area of 3115 square miles and is characterized by rich prairie soil formed by the Wisconsin, Iowan, and Kansan glacial drift. Agricultural runoff is the major source of water pollution in the Iowa River Basin, since over 90% of the area is in agricultural use. The magnitude of industrial and municipal discharge of organic pollutants into the Iowa River and its tributaries is relatively small, with Marshalltown being the only city with greater than 10 000 population existing in the basin area above the reservoir.

Coralville Reservoir is located in eastern Iowa, about 3 miles north of Iowa City. At the conservation pool level, 680 ft above sea level, it forms a lake 21.7 miles long, with a surface area of 4900 acres and a capacity of 40 300 acre ft. The reservoir is a shallow, eutrophic impoundment with extensive littoral areas where there is a close association between the zones of photosynthesis and decay. Below the reservoir, the Iowa River serves as the raw water supply for The University of Iowa and Iowa City.

Experimental

Grab samples from the Iowa River were taken at a depth of 1 ft, both upstream and downstream from the Coralville Reservoir, Iowa. The sample was centrifuged at 2000 rpm in a Damon/IEC HN-S centrifuge to remove suspended solids and was subsequently stored at 3 °C for 1 to 3 weeks.

Concentration of the samples was carried out by freeze-drying. The centrifuged sample was frozen at −20 °C and freeze-dried in a lyophilizer. A volume of 500 mL required approximately 2 days for complete removal of water. The freeze-dried residue was dissolved in 2 mL of elution water, which had been predistilled, purified with a Millipore Milli-Q system, and purged with nitrogen gas to strip THMs. It contained a 0.01 M solution of K_2HPO_4 and KH_2PO_4 to provide buffering capacity, and a 0.02% concentration of sodium azide to serve as bactericide. The pH of the elution water was 6.95. This redissolution resulted in a 250-fold increase in concentration of the nonvolatile organics. The undissolved (inorganic) solids were then removed by centrifugation.

To achieve the required fractionation of the organic compounds according to molecular weight, gel permeation chromatography with Sephadex (Pharmacia Fine Chemicals, Uppsala, Sweden) dextran gels was performed. Sephadex G-75 was utilized with an upper exclusion limit of 50 000 and a lower exclusion limit of mol wt ~1000.

The columns were constructed of polyethylene with brass fittings and Teflon tubing. Column dimensions were 2.2 cm × 60 cm with a bed volume of 164 mL. Columns were operated downflow at a rate of 40 mL/h with a constant head of 50 cm.

Calibration of the columns required protein compounds of known molecular weight including: bovine serum albumin (BSA) monomer, mol wt 66 500; ovalbumin, mol wt 43 500; trypsinogen, mol wt 23 560; cytochrome *c*, mol wt 12 380; and bacitracin, mol wt 1500. Blue dextran 2000, with a mol wt of 2×10^6, was used to determine the void volume of the column. The calibration curve of Sephadex G-75 resulted in a straight line on a plot of log molecular weight vs. elution volume.

Next, the concentrated sample of 2-mL volume was injected onto the column and eluted with approximately 200 mL of elution water. Separation of the compounds was on the basis of the molecular exclusion principle; molecules are eluted from the gel in decreasing order of size. Collection of the eluant in 2.5-mL volumes was followed by measurement of total organic

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carbon (TOC) concentration. A plot was then made of TOC vs. elution volume, resulting in a chromatogram.

Following fractionation, the 2.5-mL elution samples were combined into groupings of various molecular weight ranges and stored in acid-washed flasks at 3 °C. The number of molecular weight fractions varied from four to nine per sample.

For sample chlorination, an attempt was made to simulate chlorination conditions at The University of Iowa lime-softening water treatment plant, which chlorinates to a free chlorine residual concentration of 1.5–2.5 mg/L. Duplicate 10-mL samples were prepared from a size fraction containing a high TOC concentration. The pH of one of the duplicate samples was adjusted upward to 10.8 (from ~7), by adding 0.02 mL of 0.02 N NaOH (Baker Analyzed Reagent grade). This is a typical pH found during the course of lime softening at the University plant. The sample was then chlorinated with 6 mg/L Cl by addition of NaOCl solution (Fisher Scientific Co., 4–6% NaOCl, Laboratory grade). The chlorine solution was applied with a 100-μL Hamilton gas tight syringe, accurate to 1 μL, and checked with an *o*-tolidine–arsenite (OTA) test after 5 min to confirm a 2 mg/L free residual. The drop in pH following the addition of NaOCl was found to be negligible. The remainder of the sample fractions were chlorinated in the same manner, using this dosage. The chlorinated sample fractions were then stored in the absence of light at 3 °C and allowed a reaction time of approximately 10 h, to simulate the distribution system.

A Tracor Microtek MT-220 gas chromatograph (GC) equipped with a nickel-63 electron capture detector was used for qualitative and quantitative THM analysis. The 6 ft × 0.25 in. U-shaped glass column was packed with 4% SE-30 and 6% OV-210 on 80/100 mesh Gas-Chrom Q Support. High purity nitrogen was employed as the carrier gas. The instrumental parameters for gas chromatographic analysis were as follows: carrier gas flow rate, 40 cm^3/min; column temperature, 70 °C; inlet temperature, 230 °C; detector temperature, 245 °C; and attenuation, 32×10^2.

Standard solutions of each of the four THMs were made up in THM-free water (predistilled, purified with a Millipore Milli-Q system and purged for 2 h with high purity nitrogen gas).

A minimum of four standards were used to plot the calibration curve (peak height vs. concentration) for each haloform. Prior to analysis for THMs, it was necessary to make a series of dilutions of each chlorinated sample to ensure that the concentrations would fall in the linear range on the calibration curve. The dilution water contained 4 mg/100 mL ascorbic acid (Baker Analyzed Biochemical Grade, J. T. Baker Chemical Co.) to provide a stoichiometric excess of reducing agent to dechlorinate the samples and prevent any remaining residual chlorine from reacting with trace organic precursors in the THM-free dilution water. The ascorbic acid in no way interferes with THM analysis via electron-capture gas chromatography (*9*).

THM analysis was then conducted on dilutions of the chlorinated samples by a liquid extraction method (*10*). THMs were determined in a 3-μL aliquot of the pentane-extracted phase by gas chromatography.

To avoid potential problems with contamination, the purity of the pentane and cleanliness of the glassware used in this analytical procedure were of primary importance. It was found that even spectrophotometric grade pentane may contain interfering peaks at low concentrations. However, lot numbers of pentane were located with acceptable contamination levels. All glassware was rigorously cleaned with chromerge, rinsed with THM-free water, and dried in a 200 °C oven. Frequent blank runs were performed to ensure the absence of artifacts

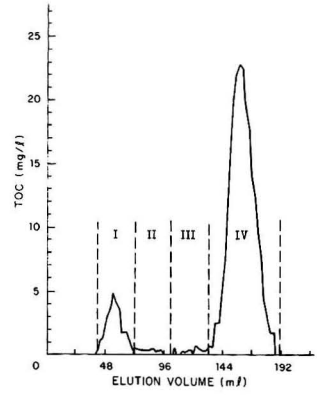

Figure 1. Chromatogram showing fractions chlorinated for Oct 10, 1977, Iowa River, G-75 column

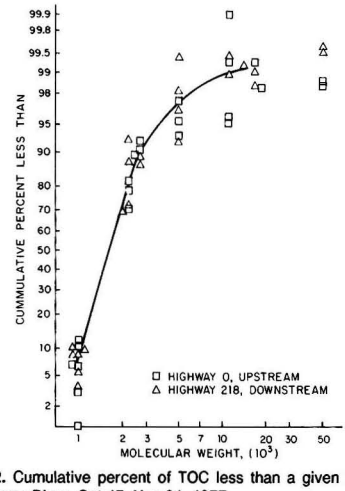

Figure 2. Cumulative percent of TOC less than a given molecular weight, Iowa River, Oct 17–Nov 21, 1977

and background contamination. Details of experimental procedures are given by Nitzschke (*11*) and Lucas (*12*).

Results and Discussion

An example of a chromatogram is shown in Figure 1 from a sample of the Iowa River upstream from Coralville Reservoir on Oct 10, 1977. Note the first peak in TOC ranged from 40 to 72 mL and corresponds to organic compounds with molecular weights greater than 50 000. This first peak decreased sharply after Oct 10, and the percentage of organics greater than mol wt 50 000 decreased from ~15 to less than 2% of the total TOC present in the concentrated sample. The decrease in large organic compounds may have been caused by a seasonal decline in algal productivity and autochthonous organics and/or a decrease in runoff of allochthonous material.

The apparent molecular weight distribution of TOC was determined from the calibration curve of the G-75 column. As seen in Figure 2, approximately 1.0% of the TOC was greater than mol wt 50 000, 90% was less than mol wt 3000, and 7% was less than a mol wt of approximately 1000. Therefore, a great majority of organics in the Iowa River during November and December 1977 were compounds of relatively low molecular weight, between 1000 and 3000 g/mol.

Table I. THM Formation and Chloroform Yield as a Function of Precursor Molecular Weight Range for Iowa River, December 1977–January 1978

sample	app mol wt range	TOC, mg/L	$CHCl_3$, ppb	$CHCl_2Br$, ppb	$CHBr_2Cl$, ppb	$CHBr_3$, ppb	yield, $\mu g\ L^{-1}$ $CHCl_3$/ $mg\ L^{-1}$ TOC
blank			3.4	<0.2	<0.2	<0.2	
I	>50 000	0.05	4.4	0.4	<0.2	<0.2	2.00
II	−33 000	0.30	5.4	0.3	<0.2	<0.2	6.67
III	−20 000	0.55	4.2	0.4	<0.2	<0.2	1.33
IV	−10 000	0.48	4.6	0.3	<0.2	<0.2	2.40
V	−6 000	0.60	4.2	0.3	<0.2	<0.2	1.33
VI	−3 000	2.23	15.0	1.4	<0.2	<0.2	5.27
VII	−1 700	13.3	43.0	8.0	0.8	0.2	2.98
VIII	−1 000	34.8	13.0	21.0	11.0	2.1	0.28
IX	<1 000	8.30	11.5	14.3	6.0	1.8	1.01
	total[a]	61.1	74.7	46.4	17.0	3.9	1.22

[a] Total excluding the blank; sample concentration factor ~2.5; G-75 Sephadex column.

Losses of organics in the concentration step were considerable. The recovery of the TOC in the original sample after freeze-drying concentration was approximately 70%. It was determined that nearly 100% recovery could be achieved if the sample was only partially lyophilized, i.e., not taken to complete dryness. One sample was concentrated by vacuum rotoevaporation at 35–40 °C with a recovery of 81.4%; however, 100% was recovered if the TOC of the condensate was included in the calculation. Apparently, the losses of organics occurred primarily due to volatilization of organics. Therefore, this work dealt with nonvolative and semivolatile substances. Most volatile losses occur from organic compounds of 3–5 carbon atoms according to Andelman and Caruso (*13*). Carbon could also have been lost in the redissolution of the freeze-dried residue, and approximately 5% of the organics were lost by adsorption to the Sephadex gel. This is within the range of 0–13% reported by other investigators for natural waters (*14, 15*).

The molecular weight fractions for 16 samples were chlorinated to determine the yield of THMs. Tabular results (Table I) are presented for a December–January composite of grab samples. Elution water blanks were identically chlorinated to serve as a control. Yields of chloroform were calculated as $\mu g/L$ $CHCl_3$ per mg/L TOC, with 10 000 being the theoretical stoichiometric maximum. The high $CHCl_3$ yield from sample fraction II (mol wt 50 000–30 000) may have been due to contamination at low levels, since it is the only fraction which is inconsistent with yields from the high molecular weight fractions in other samples. Neglecting this possible error, the table then shows that the highest $CHCl_3$ yield occurred in sample division VI (mol wt 6000–3000), with a lesser amount in sample fraction VII (mol wt 3000–1700). The haloform, bromodichloromethane, was also produced along the entire spectrum, although at less than 1 ppb in the larger molecular weight groups.

The pattern of occurrence for the four THMs in this composite sample, as a function of molecular weight, confirmed trends observed in the 15 other samples. Fifteen parts per billion of chloroform was detected at mol wt 6000–3000. Organics with mol wt 3000–1700 produced the highest concentration of $CHCl_3$, 43 ppb, and also significant concentrations of $CHCl_2Br$ and $CHBr_2Cl$. In sample fraction VIII (mol wt 1700–1000), the $CHCl_3$ concentration decreased to 13 ppb, along with an even greater drop in yield, and $CHCl_2Br$ and $CHBr_2Cl$ occurred at their highest concentrations, of 21.0 and 11.0 ppb, respectively. Bromoform appeared for the first time, and in its highest concentration of 2.1 ppb in this fraction. Sample division IX, which was composed of compounds with molecular weights less than 1000, produced less quantities of each of the four THMs.

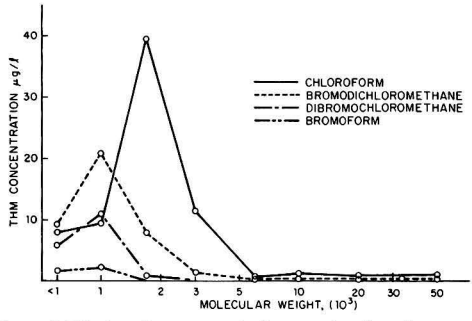

Figure 3. Trihalomethane concentration as a function of precursor molecular weight, Iowa River water, December 1977–January 1978

Figure 3 gives the THM concentrations as a function of molecular weight for the December 1977 through January 1978 composite sample. Concentrations reported are minus the blank and include a concentration factor of approximately 2.5. Primarily, THMs were formed from precursors of less than mol wt 6000. Chloroform was detected in greatest concentrations from the organic fraction of mol wt 1700–3000. At molecular weights less than 1700, bromodichloromethane was produced in the highest concentration of any THM, and dibromochloromethane and bromoform were detected in significant concentrations. The percentage contribution of the brominated haloforms is believed to be directly related to the bromide concentration of the raw water (*16*). The bromide concentration in Iowa River water was 0.10–0.45 mg/L.

Data for the 16 Iowa River samples from September 1977 through January 1978 are plotted as THM yield vs. log scale of molecular weight in Figures 4–7. Yields are plotted at the lowest molecular weight of the precursor molecular weight range. In general, chloroform was detected in concentrations greater than the blank throughout the molecular weight spectrum, but it primarily resulted from organics of mol wt less than 5000. Yields at molecular weights less than 5000 ranged from 0.0 to 10.9 $\mu g/L$ $CHCl_3$ per mg/L TOC while those at molecular weights greater than 10 000 were usually less than 2.0. Owing to low concentrations of TOC in the higher molecular weight fractions, there is less precision in the analytical measurement and yield calculation. Chloroform yields were greatest for the molecular weight ranges from 2200 to 5000 and less than 1000. The considerable scatter in the data may reflect

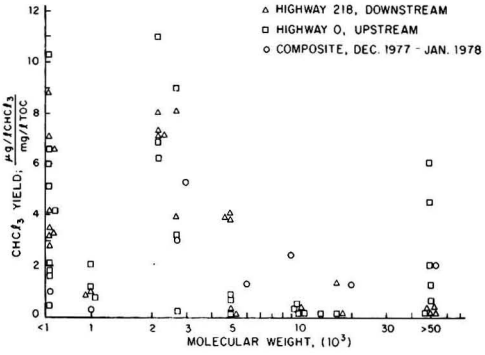

Figure 4. Chloroform yield vs. molecular weight

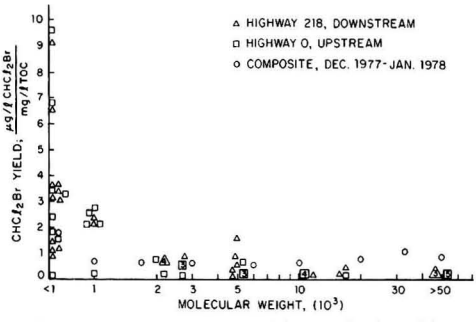

Figure 5. Bromodichloromethane yield vs. molecular weight

the functional differences in organic moieties with time, and proves that chloroform concentrations would be difficult to predict based solely on knowledge of the molecular weight and the TOC distributions of naturally occurring organics.

Figures 5–7 gives the yields for the other three THMs as a function of molecular weight for the period September 1977 through January 1978. With each bromine atom added, the mean yield decreases and the precursor organics are of lower molecular weight. The maximum yield of $CHCl_3$ was 10–11 μg/L per mg/L TOC at molecular weights of less than 5000, while the maximum yields for $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ were 9.7, 4.5, and 0.36, respectively; all were formed at molecular weights less than 1000.

On the average, 75% of the THMs formed from chlorination at pH 10.8 of Iowa River water was derived from organics of less than mol wt 3000 (Figure 8). The cumulative distribution of Figure 8 indicates that both the fraction of less than mol wt 1000 and the heavier humic substances are important in the formation of trihalomethanes. The fraction less than mol wt 1000 has been cited as including fulvic acid compounds (*8*).

Overall yields of total trihalomethanes (TTHMs) varied from 2.3 to 7.2 μg/L TTHM per mg/L TOC. There was a slight tendency for the sample from below Coralville Reservoir to cause higher TTHM yields than that above (significant at the 90% confidence level, $z = 1.9432$ in a paired t test). The effect could be due to biological degradation and sedimentation of the higher molecular weight compounds, which were generally less reactive. TTHM concentrations varied from 52 to 177 ppb with a mean of 104 ppb in samples that were concentrated 2.5 times. The effect of impoundment was not dramatic on THM formation.

The average reactant ratios plus or minus 1 SD were as follows: 0.04 ± 0.01% of the TOC present in the concentrated

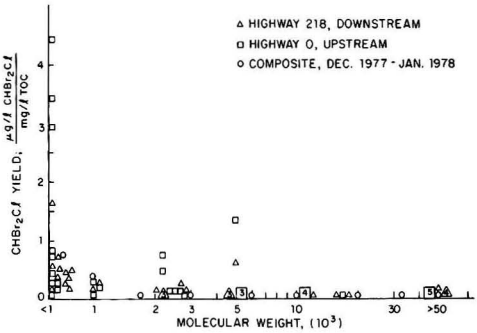

Figure 6. Dibromochloromethane yield vs. molecular weight

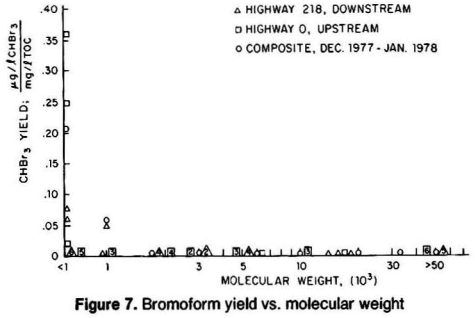

Figure 7. Bromoform yield vs. molecular weight

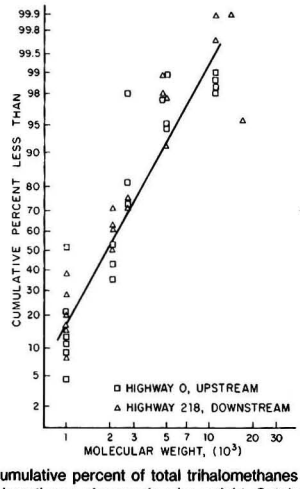

Figure 8. Cumulative percent of total trihalomethanes formed from organics of less than a given molecular weight, October–November 1977

sample reacted to form THMs; 1.1 ± 0.4% of the chlorine reacted; and 24.1 ± 11.5 μg/L of bromine reacted, between 5.0 and 20% of bromide present. As more chlorine is used in chlorination, the chlorine reactant ratio of 1.1% would be expected to decline. Reactivity is greatest for bromide, which was shown to interact with small organics (mol wt <1700) to form $CHCl_2Br$, $CHClBr_2$, and small amounts of $CHBr_3$. Hypobromous acid can be formed initially via the oxidation of the bromide ion by chlorine and has been shown to be more reactive than hypochlorous acid (*17*).

Conclusions

Ninety percent of the organics in the Iowa River during October 1977 to January 1978 were less than mol wt 3000, while approximately 7% were less than mol wt 1000. Seventy-five percent of the THMs formed were derived from organics of less than mol wt 3000, and 20% on the average were derived from compounds of less than mol wt 1000. In general, total trihalomethanes were formed in the molecular weight ranges where the greatest concentration of TOC was detected, but yields of TTHM were larger for the organics less than mol wt 1700. Chloroform was primarily a product of chlorination of precursors less than mol wt 5000, but the brominated THMs formed from smaller organics, less than mol wt 1700. Effects due to impoundment were not dramatic, but some tendency was observed for greater THM yields downstream from the Coralville Reservoir.

Acknowledgments

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Water Distribution System, a New Source of Mutagens in Drinking Waters

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■ Compounds capable of reverting base pair substitution and frame shift mutants of *Salmonella typhimurium* are introduced in some drinking waters during transportation from treatment site to the consumers.

The disclosure of the presence of halogenated hydrocarbons and other potentially carcinogenic compounds in drinking waters has caused public concern with respect to the quality of drinking waters. Generally recognized dimensions of the chemical problem in drinking waters are (a) man-made chemicals that find their way into drinking water sources from pollution and (b) compounds formed during chlorination of water supplies. The data presented here show a third and potentially important dimension of the problem, which concerns the introduction of mutagenic/carcinogenic substances in the distribution process.

Experimental

Three medium sized water supplies, each representing different raw water sources, wastes/discharges entering the raw water, treatment processes, and distribution lines, were selected for this investigation (Table I). From each water supply, four samples (raw water, finished water, and two samples from different locations within the supply network) were obtained. All the samples within a single water supply were collected on the same day and transported to the laboratory in wet ice. Samples were sterilized by filtration through sterile 200-nm Millipore membrane filters.

Concentration of chemicals from the drinking waters was performed in the field using flexible polyurethane foam columns (*1, 2*). Foam columns have been shown to effectively concentrate trace quantities of a wide variety of chemicals from water (*2–5*). Chemicals were recovered from 60 L of finished and 30 L of raw water. Following exposure to water, foam columns were wrapped in aluminum foil to protect from light and transported to the laboratory in wet ice. Each foam column was eluted successively with acetone (20 mL) and benzene (75 mL). The combined eluate was passed through a sodium sulfate bed to remove residual water and evaporated to 1 mL by rotary evaporation. The mixture was evaporated to dryness with prepurified grade nitrogen and redissolved in dimethyl sulfoxide for mutagenicity assay.

For detection of mutagens, the Ames *Salmonella typhimurium* assay (*6*), with strain TA100 as base pair substitution mutant and strain TA98 as frameshift mutant, was employed after minor modifications. Low concentrations of mutagenic substances in unconcentrated waters were determined by preparing minimal glucose agar with the test water; thus, test

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Table I. Details of the Water Supply System Studied

supply system code	geograph location	raw H_2O source	type of raw H_2O pollution	treatment provided[a]	probable nature of distribution line	sampling dates
A	Southeast	Ohio River	industrial waste and sewage	aeration with lime and ferric sulfate, phosphate, activated carbon addition, filtration, chlorination, and fluoridation	intermix of copper, cast iron, cement-lined ductile iron, and asbestos cement	2-2-78
B	Midwest	lake	papermill waste	activated carbon, lime, alum, ferric sulfate, ammonium sulfate, filtration, chlorination, and fluoridation	cement-lined ductile iron	3-13-78
C	Midwest	ground water	uncontaminated source	lime, ferric sulfate, sulfuric acid, chlorination, and fluoridation	cast iron	3-16-78

[a] Not necessarily in the proper order of treatment.

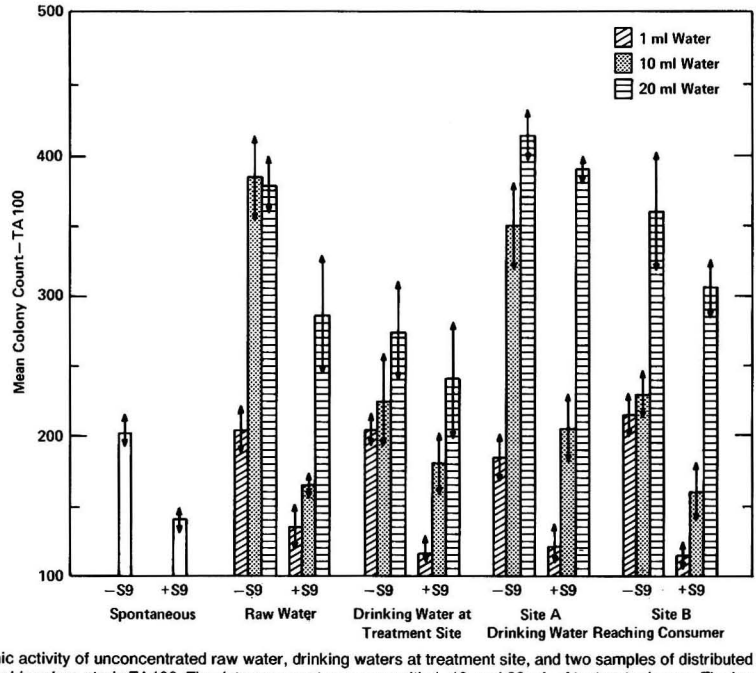

Figure 1. Mutagenic activity of unconcentrated raw water, drinking waters at treatment site, and two samples of distributed waters from supply system AP in *S. typhimurium*, strain TA100. The data represent response with 1, 10, and 20 mL of test water/assay. The increase in the number of revertants at distribution sites A and B over drinking water at the treatment site is best observed at the test water concentration of 20 mL/assay, and is significant at $p < 0.05$

water was present in the bottom agar, whereas bacteria and activation mix (when added) were present in the agar overlay. Modification of the Ames assay in this manner permitted incorporation of as much as 20 mL of test water in the assay. To substantiate the expected low reversion rates with unconcentrated drinking waters, efforts were made to obtain dose–response data. The volumes of drinking water tested were 1, 10, and 20 mL/assay. Mammalian metabolic activation of the compounds present in water was achieved by incorporating rat liver homogenate (S-9) derived from male Sprague-Dawley rats induced with Aroclor 1254. Standard S-9 addition was 50 μL/assay. Mutagenicity assays on all four water samples from one water supply were carried out simultaneously, together with a distilled–demineralized water control to determine spontaneous reversion, and positive controls using known mutagens recommended by Ames (*6*) and benzo[*a*]pyrene (5 μg/assay). The assays were performed in quintuplicate and results expressed as an average. A probability of 0.05% or less in the Student *t* distribution was considered to represent a significant increase in revertants above spontaneous.

The chemical concentrates prepared from water, using polyurethane foam plugs as sorbent, were evaluated using conventional plate incorporation assays and spot tests with *Salmonella* strains TA100 and TA98 as described by Ames (*6*). Studies showed that mutagens and/or toxicants were not introduced in detectable quantities from the solvents used for column elution and from polyurethane foam. Due to limitation on the volume of the concentrate, the assays were performed in duplicate only.

Results and Discussion

Assay of the unconcentrated raw, treated, and distributed water samples from the water supplies coded as AP and CH revealed that mutagens were being contributed by the distribution process (Figures 1 and 2). On the other hand, the samples obtained from the water supply coded as WH were not mutagenic to any of the tester strains (data not shown).

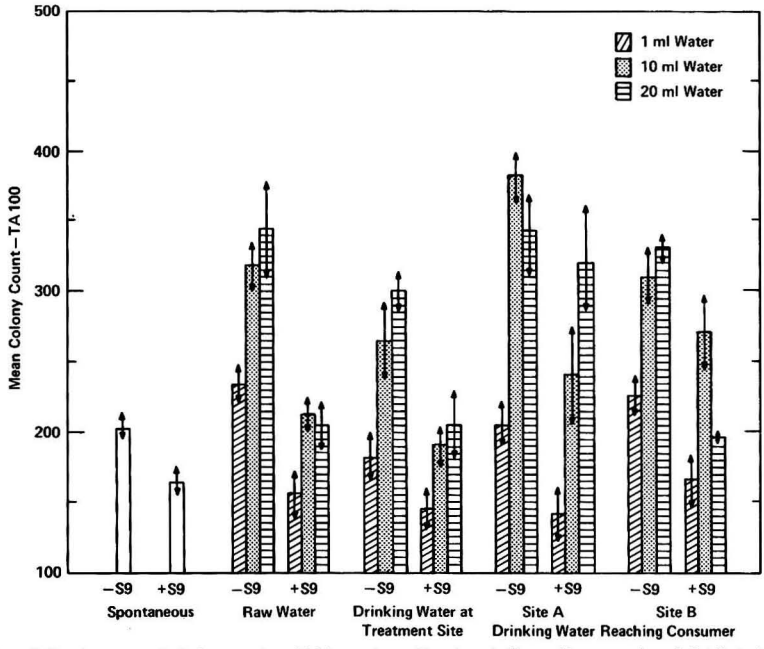

Figure 2. Mutagenic activity of unconcentrated raw water, drinking waters at treatment site, and two samples of distributed waters from supply system CH in *S. typhimurium* strain TA100. The data represent response with 1, 10, and 20 mL of test water/assay. The increase in the number of revertants at distribution sites A and B over drinking water at the treatment site was best observed at a test water concentration of 10 mL/assay (except for site A, + S9, where 20 mL of water/assay gave optimum increase). Level of significance for the increase, $p < 0.05$

The treatment processes employed at the water supplies AP and CH caused a reduction in the mutagenicity of raw waters in *Salmonella* strain TA100. However, upon passage of the treated water from these sites through distribution pipes, a consistent and significant increase in the level of mutagenicity beyond the levels found in raw waters was noted. The increase in the number of revertants attributed to the distribution process at the water supply AP was 140 for distribution site A and 85 for site B, for 20-mL sample volume. The mutagens introduced were active without liver enzyme activation. With the distributed water from the water supply CH, the increase in the number of revertants was relatively more pronounced at the test water volume of 10 mL/assay. At this concentration, the increase in revertants in distributed samples over treatment site samples was 120 for distribution site A and 45 for site B. The mutagens introduced at site A were partially inactivated by liver enzymes. However, the number of revertants at site B almost doubled in the presence of S-9, demonstrating the presence of mutagen(s) requiring mammalian metabolic activation. The dose–response profiles shown further confirm the presence of mutagenic compounds in the distributed samples. Strain TA98, which detects frameshift mutations, did not show a mutagenic response with unconcentrated waters from water supplies AP or CH in the presence or absence of mammalian metabolic activation.

None of the water samples showed detectable quantities of histidine when assayed by the enzymatic method of Hassall (7). The assay permitted detection of as low as 1 μg/mL of histidine. We feel, therefore, that the increase in the number of revertants seen is due to the presence of mutagens in drinking waters. The mutagens introduced in the distribution process are not volatile in nature (e.g., trihalomethanes, vinyl chloride, etc.), since such compounds would be lost during vacuum filtration of the test waters and/or maintenance of the minimal glucose agar prepared with test water, at 47 °C in order to pour into plates.

It might be argued that the drinking waters at the treatment site contain more residual chlorine than do the waters reaching the consumer, and this may be responsible for the reduction in the number of revertants in the treatment site sample. If chlorine was present in the water in high enough concentration to exhibit toxicity, one would expect a decrease in the number of revertants with an increase in the volume of water in the assay. The dose–response data show that this was not the case. Generally, an increase in the volume of test water in the assay was accompanied with an increase in the number of revertants. Therefore, the decrease in the number of revertants in drinking waters at the treatment site was clearly due to the removal of mutagens during treatment and not due to the influence of residual chlorine.

The organic mixtures concentrated by foam plugs from raw and drinking waters from the water supplies AP and CH were nonmutagenic to *Salmonella* strain TA100. The concentration of the organic mixtures used in the assay represented 100–1000 mL of water. High concentrations of the concentrate were toxic to the bacteria. Since mutagenic activity toward strain TA100 was detected in the unconcentrated samples, this demonstrates the inability of polyurethane foam to recover these mutagens. The organic mixture recovered from the distribution system samples of water supply CH exhibited a strong mutagenic response in strain TA98 after activation by liver enzymes (Figure 3). It should be mentioned that mutagenicity toward strain TA98 was not detected in unconcentrated samples. The mixture from as little as 100 mL of water caused a more than sixfold increase in the number of revertants in the plate incorporation assay. Mutagenic activity was not detected in the spot test, which suggests that the mutagens were nondiffusible in aqueous media. Since these mutagens

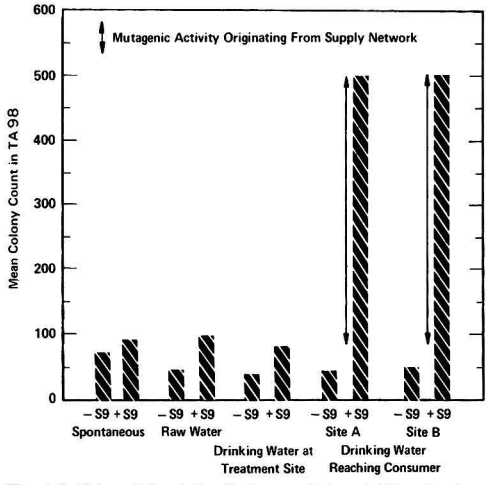

Figure 3. Mutagenicity of chemical concentrates of different waters from water supply CH. Chemicals were recovered from water by sorption on polyurethane foam columns. The data shown represent mutagenic activity with 0.1 mL of concentrate, representing 100 mL of test water/assay. An increase in the number of revertants at distribution sites A and B over drinking water at the treatment site is significant at $p < 0.05$

were not present in either raw water or finished water at the treatment site, they were clearly introduced from the distribution process. Mutagenic compounds active in TA98 were not detected in the organic concentrates prepared from the samples from water supply system AP. In agreement with the results obtained with unconcentrated waters, the organic concentrates of water from the water supply WH were nonmutagenic to *Salmonella* strains TA98 and TA100.

The data presented here show that the water distribution process is able to introduce two different classes of mutagens. One class, which responds to the base pair substitution revertible strain TA100, does not adsorb on polyurethane foam and acts without metabolic activation. Compounds of this class are probably polar and of low molecular weight since they could be detected by incorporation in the bottom agar (minimal agar). We have observed that when the Ames mutagenicity assay is performed by preparing minimal glucose agar in the test water, although it allows incorporation of large quantities of water, it becomes less sensitive toward mutagens with limited diffusibility in the aqueous media (e.g., polycyclic aromatic hydrocarbons). The second class, which responds to the frameshift mutant TA98, requires metabolic activation and can be recovered from water by adsorption on polyurethane foam. They are probably high molecular weight, nonpolar compounds, since they fail to exhibit mutagenicity in the spot test and when incorporated in the bottom agar.

Several possible events may account for increased mutagenesis in water after distribution. Mutagenic compounds could be leached from the interior surface of municipal water tanks and pipelines, which are frequently coated with coal tar, a mixture containing proven animal carcinogens. Addition of polar compounds is unlikely by this mechanism because of the expected rapid depletion of such compounds. Efforts to link the mutagenic responses reported here to the nature of the coating within the pipes in each distribution system were unsuccessful because only incomplete information could be obtained on the coating practices employed. Synthesis of mutagens during water distribution as a result of chemical reaction, e.g., reaction of residual chlorine with organics, oxidation, etc., or microbial action may also be possible. It is conceivable that distribution pipe walls may support microbial growth and these microorganisms may convert inactive chemicals into mutagens and/or synthesize new mutagens. Synthesis of some strong mutagens by microbial action has been noted in other environments (*8*).

Acknowledgment

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Mercury Removal from Water by Iron Sulfide Minerals. An Electron Spectroscopy for Chemical Analysis (ESCA) Study

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■ Using ESCA (electron spectroscopy for chemical analysis) and atomic absorption spectroscopy as analytical techniques, we show that naturally occurring sulfides are excellent adsorbers for aqueous solutions of Hg^{2+} and Hg^0. The Hg concentration in chlor-alkali effluent can be decreased dramatically to less than 100 ppt.

Mercury pollution of natural waters by man's activities (*1–3*) has created severe problems in many countries of the world. It has been estimated that the land-derived flux of mercury to the oceans is four times the preman level (*4*). In addition, an increased use of coal and geothermal steam for electrical generation will, without further abatement measures, increase mercury (and other heavy metal) contamination of the atmosphere and hydrosphere. Of particular recent ecological concern has been the mercury pollution from industrial plants and their associated dump sites (*2*).

Although mercury losses from these plants have been reduced greatly in the last decade (*5,6*), economical and efficient methods must be devised to decrease further losses to the environment. Because the solid-solution adsorption reaction is known to control many heavy ion concentrations in the environment, we looked for a common economical mineral to adsorb Hg from such industrial waste. Pyrrhotite (FeS) and pyrite (FeS_2) ores seemed ideal candidates for a number of reasons. Mercuric ions have a large affinity for sulfide, as evidenced by the solubility product for HgS and a preliminary adsorption study on heated pyrite (*7*). Iron sulfides are common and economical minerals to mine throughout the world and are usually quite accessible in localities where mercury contamination is dominant. For example, most massive sulfide mining operations (Pb, Zn, Cu) separate and discard huge amounts (thousands of tons) of iron sulfides yearly. Iron sulfide and its oxidation products should pose little pollution threat if dumped into contaminated waterways. If mercury exchanges for surface lattices sites, the displaced iron and/or sulfur is precipitated by natural processes.

Three separate sets of adsorption experiments have been carried out. In the first two experiments, 0.1 to 1.0 g of powdered (<200 mesh) pure Sudbury pyrrhotite or pyrite was stirred in deionized distilled water in polypropylene or borosilicate beakers for approximately 2 h to obtain equilibrium. The pH was adjusted to between 4 and 9. Solutions of $HgCl_2$ were added to the stirred FeS to give initial Hg concentrations between 1 and 200 ppm in a first study and 20 and 100 ppb in a second study. In the second study, large concentrations of Cl^- were added to simulate chlor-alkali waste. At selected times, 10-mL aliquots were removed and centrifuged to remove any iron sulfide powder. The samples were then analyzed for mercury by cold vapor chemical (*8*) or graphite furnace flameless atomic absorption methods (*9*).

To show the great utility of the ESCA technique for studying metal sorption on solids directly, and to study further the effect of chloride ion concentration, a third set of experiments was performed. High grade pyrrhotite and pyrite ores were cut into small pieces with a 1-cm^2 surface and then ground and polished. Each sulfide plate was washed thoroughly in acetone and deionized distilled water and air-dried prior to ESCA (XPS) analysis for surface trace impurities of silica (SiO_2), mercury, chlorine, etc. A review of this ESCA technique has been previously published (*10–12*). The theory of ESCA and its recent applications in surface analysis have been critically reviewed by Hercules (*13–15*). These plates were then placed in 500 mL of various concentrations of mercuric chloride or elemental mercury (Hg^0) at pH 4–7. After a specific time in solution, each plate was carefully removed from its reaction solution and dipped five times in fresh deionized water to remove unadsorbed, adhering Hg ions (*10, 16*). Each plate was then air-dried and analyzed using the ESCA technique for the following elements: Hg, Cl, S, Fe, C, and O.

The data for the mercuric ion uptake in the first experiment are summarized in Figure 1. The data indicate an adsorption process, as the mercury loss from solution is proportional to the weight of powdered FeS and the initial mercury ion concentration. The Langmuir adsorption expression (*17*) was used to determine the maximum adsorption capacity (X_m, 3.55×10^{-2} mol of Hg/mol of FeS) and the adsorption constant (b, 6.05×10^4) for the FeS powder. The equilibrium results fit well to the Langmuir adsorption equation and adsorption isotherm. The good linear fit to the Langmuir equation indicates a sorption process proportional to sorbent surface area and sorbate concentration at constant pH.

Table I summarizes the Hg uptake at much lower Hg contents for both Hg^{2+} and Hg^0 with FeS and FeS_2. These results are notable for two reasons. Firstly, with the exception of Hg^0 on FeS, over 95% of the Hg is removed from solution in all cases. Secondly, the adsorption is not decreased by the chloride ion concentration. This result contrasts with previous studies involving the removal of mercury from solution by other materials where increasingly greater Cl^- content reduced the mercury adsorption from solution (*18*).

The ESCA results using both pyrrhotite and pyrite plates, at a solution pH of ~4 ($HgCl_2^0$ species dominant) and variable sodium chloride content (0, 100, 1000 ppm), are shown in Tables II and III. These results show that for each initial mercuric ion concentration and constant time of reaction, the sorption rate of mercury *increased* with increasing chloride concentration, especially at low initial Hg concentrations. Mercury sorption rates on iron sulfide minerals thus do not follow a simple cation hydrolysis relationship as previously suggested for oxides (*19*). The highest Hg intensities correspond to near monolayer coverage. In the ESCA studies, little chloride and no sodium ions were detectable, although the initial solution concentration of NaCl was as large as 1000 ppm. This indicates that the mercury sorption is highly specific.

A sulfide plate studied at pH ~7 (Table II) produced a much lower sorption rate with respect to the results at pH ~4. This again indicates the pH influence upon sorption rates (see also Table I). It was also found that pyrrhotite sorbed much larger weights of mercury ions than pyrite, assuming equivalent initial mercury, sodium, and chloride ion concentrations. Thus, surface lattice sites and solubility differences are important sorption reaction parameters.

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Table I. Results of Hg^{2+} and Hg^0 Adsorption by 1-g Iron Sulfide Minerals

Hg species and mineral type[a]	pH	[Hg] initial, ppb	[Cl] initial, ppm	[Hg] final, ppb	% Hg reduction in solution
A. Hg^{2+}–FeS	4.4	20	0	0.14	99.3
	6.5	20	0	0.35	98.3
	9.8	20	0	1.00	95.0
	4.6	20	100	0.12	99.4
	7.0	20	100	0.40	98.0
	9.7	20	100	0.45	97.8
	4.4	100	0	0.57	99.4
	6.5	100	0	1.5	98.5
	9.5	100	0	4.30	95.7
	4.6	100	100	0.60	99.4
	6.7	100	100	1.3	98.4
B. Hg^0–FeS	4.5	30	0	5.1	83.0
–FeS_2	4.5	30	0	0.10	99.7
C. chlor-alkali plant waste–FeS					
CA 1[b]	5.5	2000	>1000	60	97.0
	4.4[c]	2000	>1000	40	98.0
CA 2[d]	6.2	5	<100	0.10	98.0
	4.4[c]	5	<100	0.05	99.0

[a] 100 mL of solution shaken for 1 h, and then allowed to settle 1 h before analysis of the supernatant. [b] Nontreated chlor-alkali processing water. [c] pH adjusted by dropwise addition of 1 M HCl. [d] Treated chlor-alkali processing water.

Table II. ESCA Study of Mercury Adsorption on Iron Sulfides; Variation with Chloride Concentration

init Hg concn, ppm[a]	mineral type[b]	solution pH	react. time, min[c]	Hg 4f peak area intensity ($\times 10^4$)[d] at init chloride concn, ppm		
				0	100	1000
A. Hg^{2+} reactions						
0.02	FeS	4	1440	3.6	29.4	38.7
0.10	FeS	4	5		0.42	0.47
	FeS	4	60	0.82	2.12	7.30
	FeS	4	1440	30.6	56.9	69.5
	FeS	7	1440	2.3	6.0	2.3
1.0	FeS	4	60	53.0	43.8	38.2
	FeS	4	1440	40.6	40.6	52.4
0.02	FeS_2	4	1440	1.0	7.4	9.4
0.10	FeS_2	4	1440		14.00	10.0
B. Hg^0–H_2O equilibrium reactions						
0.03	FeS	5.7	2880	2.54		
	FeS_2	5.7	5760	18.6		
	FeS_2	5.7	5760	16.0		
C. Hg^0	FeS		2880	31.3		
	FeS_2		5760	32.8		

[a] 500 mL of Hg solution used. [b] Cut pyrrhotite or pyrite ore. [c] Mineral plates dipped five times in fresh water to remove Hg solution. [d] Peak area intensity for 50 scans of Hg 4f.

Several pyrrhotite and pyrite plates reacted in elemental mercury (Hg^0) and in elemental mercury in water (Table II) were also studied by ESCA for sorption rates; pyrite appears to be a superior adsorber for Hg^0. An earlier study of Hg^0 solubility in water at 22 °C indicated an equilibrium mercury content of ~25 ppb (*20*). It is apparent that iron sulfide minerals concentrate mercury ions and atoms from extremely dilute mercury solutions, efficiently and specifically.

Process water samples (CA1 and CA2) were collected at a large chlor-alkali plant in Canada, and Hg adsorption was studied using both iron sulfide powder and plates. The adsorption results (Tables IC and III) are consistent with those using our prepared mercury solutions. The ESCA results (Table III) indicate that a significant amount of mercury in the 500-mL 5-ppb solution is removed, and the powder results (Table IC) show that this Hg content is reduced to ≤0.1 ppb. The ESCA results again indicate that the sorption rate increases with decreasing pH.

Some recent studies on mercury in fish in Quebec indicate that the natural existence of sulfide minerals, such as pyrite and pyrrhotite, may be a factor in reducing the availability of mercury to biota in otherwise sensitive areas. In contrast to

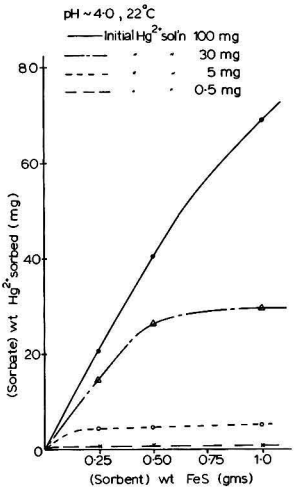

Figure 1. Mercuric ion adsorption on powdered FeS in 500 mL of solution. The time of reaction in each case is 30 min

Table III. ESCA Study of Mercury Sorption by Iron Sulfides from Chlor-Alkali Processing Waters

chlor-alkali processing solution type [a]	iron sulfide ore [b]	reaction time, h [c]	peak area intensity Hg 4f ($\times 10^4$) [d]
1. CA 1 (pH ~5.5)	FeS	1.0	1.1
		24.0	3.0
		48.0	6.9
CA 1 [e] (pH ~4.0)	FeS	4.0	nil
		24.0	4.5
		48.0	27.5
	FeS_2	24.0	7.0
2. CA 2 (pH ~6.2)	FeS	6.0	0.83
		24.0	2.10
CA 2 [e] (pH ~4.0)	FeS	4.0	27.3
		24.0	7.1
		48.0	19.3
	FeS_2	24.0	2.7

[a] As per Table II. [b] As per Table II. [c] As per Table II. [d] As per Table II. [e] pH adjusted by dropwise addition of 1 M HCl.

accepted theory, the mercury concentration in fish (*21*) was lowest in regions unaffected by point sources with the highest sediment mercury concentrations. This supposed anomaly can be explained by the presence of relatively high concentrations of sulfide minerals in the regions with the highest sediment mercury concentrations.

Our results of mercury adsorption on iron sulfides indicate the potential use in eliminating both mercuric ions and elemental mercury atoms from polluted natural waters, industrial waste, and process waters. The observed residual solution values compare to levels in ocean water (~5 ppt) and rain (~1 ppt) (*22*). A more detailed investigation involving the most efficient design of a pilot plant and related chemical parameters to best use iron sulfide ore is in progress.

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An Experimental Evaluation of Atmospheric Nitrosamine Formation

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■ It has been suggested that carcinogenic nitrosamines can be formed in the atmosphere from ambient NO_x and amines. A long-path infrared study of the reaction of dimethylamine, NO, and NO_2 has been carried out at various parts per million levels of the reactants to test this suggestion. It was found that low concentrations of dimethylnitrosamine were formed at rates independent of the amine concentration. Further experiments showed that the amine was adsorbed on the cell walls and that nitrosamine formation was probably proceeding heterogeneously. Using the data of this investigation and the results of a recent EPA study, it was shown that homogeneous nitrosamine formation in the atmosphere should not pose a significant health hazard, although further work will be required to establish whether nitrosamine formation on aerosol surfaces could result in a significant health risk.

The discovery of the suspected carcinogen (*1*) dimethylnitrosamine (NDMA) in the atmosphere in several areas of the U.S. (*2*) has led to concern that the reaction of ambient NO_x with amines to form nitrosamines could pose a health hazard. Although it was shown that airborne NDMA was due to local chemical manufacturing processes in some of these areas, it has been suggested that automotive NO_x emissions should be reduced to minimize this possible health hazard (*3*). A recent survey of several areas of the U.S. (*4*) found nitrosamine in only one location. The level found was about 0.1 ppb. The Environmental Protection Agency (EPA) has studied the reaction of NO_x and dimethylamine in air (*5*). They found that NDMA does form, but that the rate of the reaction based on amine disappearance was too slow to be of importance in the atmosphere, considering the fact that NDMA rapidly photolyzes in sunlight. The EPA study was repeated in the present work to verify their conclusions about atmospheric NDMA formation.

Experimental

The study was carried out in a long-path infrared cell (*6*) (3-m base path, 614-L multiple-reflection stainless steel) at a temperature of 35 °C and a total pressure of 760 Torr. Dimethylamine was an Eastman Kodak product, and dimethylnitrosamine was a product of Chemical Procurement Laboratories. Nitric oxide was a Matheson product, while nitrogen dioxide was prepared on the vacuum line by the thermal oxidation of nitric oxide. The concentrations of NDMA and dimethylamine were determined by measuring their infrared absorptions at 9.9 and 8.7 μm, respectively.

Results and Discussion

Various mixtures of dimethylamine (DMA), NO, and NO_2 were reacted in the dark. The disappearance of dimethylamine and the formation of dimethylnitrosamine were studied. The results are given in Table I.

In every experiment, NDMA was observed in substantially smaller amounts than the amount of dimethylamine lost. The NDMA formed amounted to an average of 6.3% of the lost amine in dry air and 7.3% in the presence of 2200 ppm of added H_2O. Examination of the corresponding concentration vs. time plots provides further insight into the chemistry of

Table I. Reaction of Dimethylamine, NO, and NO_2 in Air[a]

$[DMA]_0$, ppm	$[NO]_0$, ppm	$[NO_2]_0$, ppm	$[DMA]^b$ loss, ppm	[NDMA], ppm
4.8	2.0	1.2	1.99	0.15
13.5	2.0	1.9	3.91	0.23
7.2	2.1	2.0	5.90	0.38
3.7	2.0	2.0	2.91	0.15
5.1[c]	2.1	2.0	1.75	0.15
7.5[c]	2.0	1.9	5.45	0.20
4.0[c]	2.0	2.0	2.70	0.26

[a] Reactions carried out in the dark at 35 °C and 760 Torr total pressure for 100 to 400 min in cylinder air. [b] Refers to DMA that disappeared from the gas phase. [c] Experiments carried out in the presence of 2200 ppm of added H_2O.

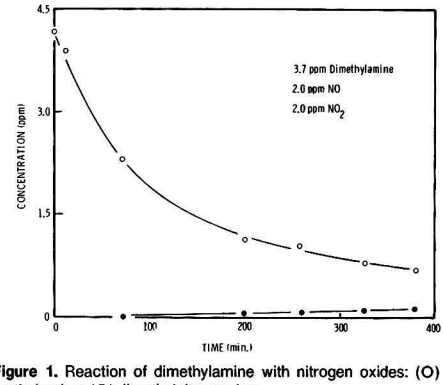

Figure 1. Reaction of dimethylamine with nitrogen oxides: (O) dimethylamine; (●) dimethylnitrosamine

NDMA formation in these systems. A typical plot is given in Figure 1. After an induction period of about 40 min, NDMA formation proceeds at a constant rate for the remainder of the reaction period, while the amine concentration decreases by about 80%. This behavior is inconsistent with that of a homogeneous gas-phase reaction. Rather, the data in Figure 1 are consistent with a mechanism involving adsorption of the amine on the cell walls, followed by NDMA formation and subsequent desorption. It was verified that dimethylamine adsorbs on the cell surfaces by carrying out a control experiment. The amine (10.2 ppm) was added to the cell, and the same rate constant for amine disappearance was observed independent of the presence or absence of added NO_x. Thus, the amine adsorbs on the cell wall and then probably reacts with nitrous acid, formed from NO and NO_2 dissolved in the water layer at the surface (adsorbed from trace amounts of H_2O in the cylinder N_2 and O_2), according to Reaction 1:

$$HNO_2 + (CH_3)_2NH \rightarrow (CH_3)_2NNO + H_2O \quad (1)$$

The nitrosamine then desorbs from the wall into the gas phase where it is detected. The constant rate of NDMA formation would then correspond to the rate of desorption. The "missing" amine undoubtedly is adsorbed on the walls either as the

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amine, NDMA, or other (unknown) products.

Grossly, the results of this investigation agree with those of the recent EPA study (5). In that study, dimethylamine disappeared from the system while NDMA was formed. The EPA investigators did not calibrate their system for NDMA, but merely *assumed* that one molecule of NDMA was formed for every molecule of amine that disappeared. They did not investigate the possibility of heterogeneous reactions. The conclusion of their study stated that the rate of homogeneous NDMA formation in the atmosphere was insignificant, based on their rate data. Since the results of the present study have shown that NDMA formation occurs at only 6 to 7% of the rate of amine disappearance, these results not only support this conclusion, but also strengthen it.

It is possible that nitrosamine formation could occur on the surface of airborne particulate matter, since the heterogeneous nature of the reaction has been demonstrated in the present study. In general, the low levels of atmospheric amines would tend to militate against this possibility. In local areas of high atmospheric amine content (sewage disposal plants, stockyards, etc.), this possibility cannot be completely disregarded. However, the results of a recent study (7) have shown negligible quantities of NDMA in the atmosphere of a sewage-treatment plant near Baltimore, Md.

Acknowledgment

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Organochlorine Insecticide Residues in Deep Sea Fish from 2500 m in the Atlantic Ocean

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■ Eleven organochlorine insecticide residues were measured in the livers of *Antimora rostrata*, a deep sea fish collected from 2500 m in 1972, 1973, and 1974 off the east coast of the United States. Compounds present were *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, *o,p'*-DDT, and dieldrin, while six compounds were not detectable. The ratio of *p,p'*-DDT to *p,p'*-DDE decreased from 2.17 in 1972 to 1.00 in 1974. The mean concentration of total DDT residues in the fish livers for the entire period was 7.06 mg/wet kg, similar in magnitude to the concentration of DDT residues found in lipid-rich livers of Atlantic cod (*Gadus morhua*) from shallow waters of the Atlantic coast of Canada.

Organochlorine insecticide residues have spread over the face of the globe to the extent that they are detectable in the biota of both poles. Initial analyses of one deep ocean fish by Teal (*1*) and a few by Meith-Avcin et al. (*2*) reveal that the lipid-rich deep sea fish have detectable concentrations of some organochlorine compounds. A 1971 National Academy of Sciences report entitled "Chlorinated Hydrocarbons in the Marine Environment" (*3*) predicted that 25% of all the organochlorine material produced would eventually enter the ocean; in the same year, Woodwell et al. (*4*) presented a global flux model that predicted the organochlorine concentrations in the atmosphere, ocean, and sediments through the end of this century. The Woodwell model (*4*) is now recognized as having some incorrect assumptions because of the limited data available at that time, and modified predictions have been made by Bidleman et al. (*5*) and others using recent data. One theme of the NAS report and the Woodwell model (*4*) is that the deep ocean sediment will be the major final accumulation site of the organochlorine compounds that enter the atmosphere. The proportion of the total material that will reach this reservoir and the rate of degradation in seawater and sediments remain in doubt, but the importance of the deep ocean sediments as the final reservoir seems undisputed (*5–7*).

Species of bathydemersal fish such as *Antimora rostrata* are permanent residents of great depths, and they feed by rooting in the sediment for infaunal animals (*8*) and cropping epifaunal animals. These fish are exceptionally rich in lipids; the livers of *Antimora rostrata* are 85% lipid on a dry weight basis (*7*). Organochlorine compounds in the prey and in the sediment ingested along with prey would be partitioned into the lipid fraction of these long-lived and slowly metabolizing fish. *Antimora rostrata* is found throughout the world's oceans at depths of 1000 to 3000 m (*9–11*), and at greater depths other species with similar lipid content and feeding habits are present. The final accumulation of organochlorine residues in deep ocean sediments and the properties of the fish living there suggest that the lipids of deep sea fish may be a reservoir that should be specifically considered in organochlorine flux models. This note reports the concentration of organochlorine insecticide residues in *Antimora rostrata* collected from a single location on 3 successive years to document the insecticide levels present in this species of deep sea fish.

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Experimental Procedures

The fish analyzed for this study were collected in July of 1972, 1973, and 1974 from a depth of 2500 m off the east coast of the United States. The collection site was 34°18.2′N and 75°32.6′W, which is beneath the mean axis of the Gulf Stream and on the upper continental rise about 50 km southeast of Cape Hatteras. The fish were collected by a standard otter trawl net; the net tows lasted 2 h and covered a distance over the bottom of 4 to 10 km. As the trawl was brought on board, the cod end of the net was prevented from touching the vessel's side or deck and the contents of the cod end were dumped into enamel pans. The fish were sorted and each one was frozen in aluminum foil at −80 °C in an ultralow temperature freezer.

In the laboratory the livers were dissected out and a 20 to 30 g piece was prepared for extraction according to the procedure given in Duke and Wilson (*12*). The tissue was extracted for 4 h with hexane in a Soxhlet apparatus. Extracts were concentrated and partitioned with acetonitrile. The acetonitrile was evaporated to dryness at 38 °C, and the residues were eluted from a Florisil column. The 6% ethyl ether in petroleum ether eluate was analyzed for aldrin, *p,p′*-DDD, *p,p′*-DDE, *o,p′*-DDT, *p,p′*-DDT, heptachlor, heptachlor epoxide, lindane, and mirex, while the 15% ethyl ether in petroleum ether eluate was analyzed for dieldrin and endrin. Residues were identified and quantified from electron-capture gas–liquid chromatograms. Most analyses were done using a column of DC-200. A second column of mixed QF-1 and SE-30 was used to confirm the identification of dieldrin and *p,p′*-DDD. Pesticide extraction *p* values were used for residue identity confirmation as suggested by Bowman and Beroza (*13*). Additional confirmation of residues and analysis of PCB compounds were obtained from subsamples of two livers of the same *Antimora rostrata* analyzed by R. W. Risebrough, Bodega Marine Laboratory.

Operating conditions for the Varian Aerograph gas chromatograph, Model 2840, were as follows—columns: 1.8 m × 6.4 mm o.d. (2 mm i.d.), Pyrex glass, packed with 3% DC-200 and a 1:1 ratio of 6% QF-1 and 4% SE-30 all on 60/80 mesh Gas-Chrom Q; temperature: injector and detector, 210 °C; oven, 180 °C; carrier gas: prepurified nitrogen at a flow rate of 60 mL/min.

The lower limit of detectability for the residues in the fish livers was 0.01 mg/wet kg. Recovery rates were determined to be greater than 85% for all the residues found in the livers, but the data reported here do not include a correction for percent recovery.

Results and Discussion

Six compounds (aldrin, heptachlor, lindane, endrin, heptachlor epoxide, and mirex) were not detected in the *Antimora rostrata* livers. The concentrations of the five compounds that were detected are given in Table I.

Relatively large proportions of undegraded *p,p′*-DDT and *o,p′*-DDT were present in the *Antimora rostrata* livers in 1972, indicating that these compounds were relatively rapidly transported to the benthic environment. Since *Antimora rostrata* does not occupy depths shallower than 500 m, the residues present in these fish must have been transported to depth before accumulation in fish. Giam et al. (*14, 15*) reported that in coastal fish from the Gulf of Mexico the ratio of *p,p′*-DDT to *p,p′*-DDE decreased from 2.8 in 1971 to 0.16 in 1974. The decrease in this ratio was interpreted by Giam et al. to indicate that the supply of undegraded *p,p′*-DDT was reduced between 1971 and 1974, but that continual degradation in the marine environment occurred. In the deep sea *Antimora rostrata*, the ratio of *p,p′*-DDT to *p,p′*-DDE was 2.17 in 1972 and decreased to 1.00 in 1974.

Table I. Organochlorine Insecticide Residues in mg/Wet kg in *Antimora rostrata* Livers

specimen no.	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	*o,p′*-DDT	ΣDDT	dieldrin
			1972			
30	1.98	0.77	4.54	0.24	7.53	0.03
31	0.69	0.35	1.76	0.13	2.93	0.02
32	1.56	0.67	2.81	0.29	5.33	0.01
33	1.58	0.69	3.48	0.18	5.93	0.01
$\bar{X}$	1.45	0.62	3.15	0.21	5.43	0.02
s	0.54	0.19	1.17	0.07	1.91	0.01
			1973			
404	1.14	0.35	1.46	0.12	3.07	0.01
405	0.55	0.21	0.79	0.07	1.62	0.01
407	3.28	0.65	2.61	0.20	6.74	0.03
$\bar{X}$	1.66	0.40	1.62	0.13	3.81	0.02
s	1.44	0.22	0.92	0.07	2.63	0.01
			1974			
400	0.58	0.27	1.34	0.13	2.32	0.01
402	2.53	0.72	2.70	0.21	6.16	0.03
403	12.45	2.48	11.58	0.80	27.31	0.01
$\bar{X}$	5.19	1.16	5.21	0.38	11.93	0.02
s	6.37	1.17	5.56	0.37	13.46	0.01

There is very little information for direct comparison with our *Antimora rostrata* data, since few deep ocean organisms have been analyzed for pesticide residues. Teal (*1*) reported a concentration of 1.13 mg/wet kg of *p,p′*-DDE in a rattail fish, *Nematonurus armaturus*, collected from 5500 m in the western North Atlantic at 25°N latitude and 62°W longitude in 1974. This concentration is similar to the range of *p,p′*-DDE concentrations, 1.45 to 5.19 mg/wet kg, measured in *Antimora rostrata* from 2500 m.

The PCB concentrations in the *Antimora* livers were analyzed by Risebrough et al. (*7*); the livers contained about 1/3 as much PCB as total DDT (DDE + DDD + DDT); the PCB concentrations were 3.8 to 12.5 μg/lipid g. We do not believe that the presence of the lower levels of PCB in our *Antimora* samples significantly interfered with the quantitation of the insecticide residues. Duke and Wilson (*12*) did not find PCBs to interfere with their quantitation of DDT and its metabolites in fish livers. Also, Sims et al. (*16*) found that ΣDDT analyses of cod fish tissues that had included compensation for the presence of PCBs gave results that were an average of 26% lower than analyses of aliquot samples not compensated for PCBs.

Organochlorine residues in cod livers from the Atlantic coast of Canada determined by Sims et al. (*16, 17*) had a mean concentration of total DDT residues of 5.6 mg/wet kg compared with the mean concentration in the livers of *Antimora rostrata* of 7.05 mg/wet kg. The similarity of the mean concentrations is striking, since the cod inhabit relatively shallow continental shelf waters. In the cod livers analyzed by Sims et al. (*16, 17*), there were increases in residues in fish that were collected from waters near large population centers such as Halifax, Nova Scotia. It would be possible to collect *Antimora rostrata* from 2500 m at various sites along the continental margin of the east coast of North America to determine whether or not population centers such as New York were affecting the concentration of residues in the fish on the adjacent deep sea. We predict that an elevation associated with population centers would not be detectable because strong horizontal dispersion of residue concentrations by the currents that parallel isobaths and sweep the continental margin (*18*) would eliminate such horizontal heterogeneity along the coast. The amount of information available on the insecticide residue content of bathydemersal fish is meager; only 11 indi-

vidual deep sea fish have been analyzed. In view of the importance assigned to deep sea sediments as the final accumulation site of these compounds, the lipid-rich fish that live in close association with those sediments merit attention.

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Received for review December 11, 1978. Accepted June 29, 1979. The Duke University Cooperative Oceanographic Program provided shiptime on R/V Eastward through National Science Foundation Grants GA-27725 and GD-32560; research support was through National Science Foundation Grant No. GA-28742. Reference to trade names does not imply endorsement of the product by the National Marine Fisheries Service, NOAA.

CORRESPONDENCE

SIR: In your February issue, C. Chakoumakos, R. C. Russo, and R. V. Thurston present 96-h LC_{50} acute copper toxicity data for "Cutthroat Trout (*Salmo clarki*) under Different Conditions of Alkalinity, pH, and Hardness" under nine combinations of these parameters (*ES&T*, **13**, 213–9 (1979)). Data of this type are of great interest because they are cited by the EPA in regulatory actions, standards and guidelines, and environmental risk classification of chemicals. However, there are enormous differences between the effects of copper and other essential trace metals observed in these tests and those on aquatic life in the real environment.

The reason for such differences may be found in the conditions of the experiment, which are not designed to replicate anything in nature nor to indicate the actual risk to the environment, but are designed to place chemicals into neat and tidy categories for regulatory administrative purposes. It must be noted that, under the test conditions, the copper compounds in the water are highly unstable and undergo reactions of hydrolysis, association and precipitation. Specifically, in these tests a strong solution of a copper salt is mixed continuously with the water entering each experimental tank. The mean holding time in each tank was only 5 h, during which time from 8 to 22% of the copper was precipitated, according to Table III. This table indicates that the percentage of copper precipitated correlates poorly with alkalinity, hardness, or pH. This seems to betray evidence of inadequate experimental control.

Even overlooking this uncertainty, the practical application of such data appears to be limited to a situation such as that in a stream receiving a discharge of soluble copper. The toxicity data would then apply within a stream length representing the flow of water in 5 h. At points more remote from the point source, there would be a further reduction of copper concentration and a further change of speciation of the copper accompanied by a reduction of toxicity.

Because of the instability of the copper species under the experimental conditions of this study, the entire analysis of metal speciation in this publication is suspect, as is the attribution of degrees of toxicity to these species.

There are published studies by competent investigators of toxic effects of metals under natural environmental conditions on numerous aquatic species. One wonders what purpose is served by highly contrived test conditions that appear to be favored by regulatory agencies. These place an undue onus on minor discharges or spills that are, in fact, of little actual consequence to the environment.

In conclusion, I would like to suggest that a possible reason for the inability to control the rate of precipitation of copper in these experiments may be the presence of uncontrolled small amounts of suspended matter in the water. Suspended particles behave as nuclei for precipitation. Suspended matter is always present in natural waters and it greatly reduces the toxic risk of copper to aquatic life.

S. B. Tuwiner

50 East 41st St.
New York, N.Y. 10017

SIR: Dr. Tuwiner appears to raise two points about the subject paper. The first relates to a time factor required to reach equilibrium and the transitory nature of that equilibrium in natural environments. Equilibrium for the copper system studied was effectively attained far short of the tank water residence time. We based our calculations on the total soluble copper under the conditions specified.

His second point relates to oversimplifications of the complexities of natural aquatic systems that result from placing chemicals "into neat and tidy categories for regulatory administrative purposes". We believe Tuwiner is expressing recognition of a point already illustrated in the subject paper.

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ES&T

INDUSTRY TRENDS

Matthey Bishop, Inc. (Malvern, PA) has dedicated its new $10 million Catalyst Systems and Equipment Division facility.

Moore Systems, Inc. (San Jose, CA) has shipped the second of three computer systems to the Metropolitan Water District of Southern California.

Neptune AirPol Inc. (Englewood, NJ) will furnish 4 venturi scrubbers to pulp/paper mills; they will control emissions and collect valuable salt cake at the rate of 20 lb/t of pulp processed.

Air Products and Chemicals, Inc. will supply to Indianapolis, IN, the largest U.S. wastewater disinfection system to use ozone to complement an OASES® oxygen-activated sludge system. Startup is scheduled for 1981. Capacity is 6380 lb/d of ozone.

Peabody International has acquired Spunstrand, Inc. (Seattle, WA), a manufacturer of filament-wound ducting for the ventilation and mining industries.

Research-Cottrell's Hamon Cooling Tower Division will design/construct a $1.4 million cooling tower for Colonial Pipeline Co., near Atlanta, GA. It will be a 3-cell, mechanical draft facility to cool 56 000 gpm.

Barnard and Burk, Inc. (Pasadena, CA) and **Energy Recovery Research Group** (Portland, OR) have embarked on a project to convert scrap tires into usable energy products, along with other solid wastes. A proprietary pyrolysis technique is the key.

Continental Controls & Equipment Co., Inc. (East Brunswick, NJ) has purchased the Allith Liquid/Liquid Separator Division of Smith-Jones, Inc., and is marketing a separator that the firm says meets EPA requirements.

General Resource Corp. (Hopkins, MN) says that its Air Purification Methods subsidiary has developed a new, energy-efficient dust filter. A 75% power requirement reduction, with a 99.9% collection efficiency, is claimed.

Peabody N.E. will be general contractor for the Taunton, MA, water treatment plant; contract value is nearly $6.3 million. Capacity will be 12 million gpd of drinking water.

Scientific Systems Services, Inc. (SSS) has purchased land near Melbourne, FL, to design, develop, make, and test computer software systems for pollution control and other applications.

Chem-Nuclear Systems, Inc. (Bellevue, WA) has a $1.8 million contract to work on a process to purify contaminated water in the containment building of Three Mile Island (PA) Unit 2.

Mitsubishi Heavy Industries, Ltd. (Japan) will provide incineration facilities and a steam turbine generator to the Yokohama Municipal Government; the steam will deliver 11 500 kW of power.

Versar, Inc. (Springfield, VA) has formed the Environmental Planning Division out of what was its former wholly owned subsidiary, EnviroPlan, Inc.

Analytical Bio Chemistry Laboratories, Inc. (Columbia, MO) is offering services in contract aquatic toxicology and other related fields.

Dames & Moore (Toronto, Canada) developed criteria to be used in selecting sites for fossil and nuclear power plants, for the Canadian Dept. of Environment.

Environmental Testing Services, Inc. (Roanoke, VA), a firm specializing in SO_2 removal and fabric filter consultation, has been purchased by John McKenna and Gary Greiner, and will continue activities as before.

The Atomic Industrial Forum (Washington, DC) warned that, without nuclear power, the gasoline lines of mid-1979 could have been much worse, and said that nuclear "displaced" needs for 470 million bbl of oil for last year.

Clevepak Corp. (White Plains, NY) has changed the name of its wastewater aeration system manufacturing unit to Aerocleve Division.

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Biospherics Inc. (Rockville, MD) has expanded its laboratory services to provide aquatic toxicology testing for industrial clients, crediting EPA guidelines with the need for such expansion.

Olin Corp. (Stamford, CT) will increase its capacity to produce HTH® dry chlorinator swimming pool chemicals by 45 million lb/y, in a $40 million plant expansion at Charleston, TN.

Vestal Laboratories (St. Louis, MO) says that there is a commercially available cooling tower additive, which is known as Ty-Ion® A-35, that effectively kills the bacteria that are supposed to cause Legionnaires Disease.

The Syracuse Research Corp. (Syracuse, NY) has received a 3-year, $300 000 grant from the National Institutes of Health to study the fate and action of dichlorobenzidine in mammals.

Southern California Edison Co. and **Riverside Cement Co.** have agreed on a power cogeneration project that should eventually save the equivalent of 197 600 bbl/y of imported oil.

From the **solar energy industry,** 20 companies have submitted proposals to the Solar Energy Research Institute (Golden, CO) to build the world's largest photovoltaic power system for two small villages in Saudi Arabia.

Aeroglide Corp. (Raleigh, NC) has installed the first industrial drier specifically adapted for the drying of green sawdust and whole tree chips as an economical fuel.

Research-Cottrell has a $15 million contract to design/engineer/fabricate/construct the largest fabric filter system purchased in the U.S. to date—nearly 13 000 bags—for Houston Lighting and Power Co.

LFE Environmental Analysis Laboratories (Richmond, CA) has an EPA qualification to analyze bulk asbestos samples for school districts in the U.S.

Stone & Webster Engineering Corp. (Boston, MA) will design/build a facility that will allow Great Northern Paper Co. (East Millinocket, ME) to burn bark and other waste products and save more than 400 000 bbl/y of oil.

Brown and Caldwell Consulting Engineers has designed a $12.5 million expanded sludge handling project, which has been accepted by the City of Portland, OR.

Flakt, Inc. and **Flakt Canada Ltd.** have five contracts for a unique pneumatic dense-phase ash and dust conveying system (DEPAC); total value is $3 million. They will be used at power plants.

Chicago Bridge & Iron Co. (Oak Brook, IL) will purchase the Environmental Equipment Corp. (Austin, MN). Terms were not disclosed.

Apollo Technologies Inc. is the new name for Apollo Chemical Corp. The company is headquartered at Whippany, N.J.

Gilbert/Commonwealth (Jackson, MI) will conduct energy studies, for the Dept. of Energy, at gaseous diffusion plants located at Portsmouth, OH, and Paducah, KY.

Environmental Data Corp. (Monrovia, CA) has become a wholly owned subsidiary of Thermo Electron Corp. (Waltham, MA).

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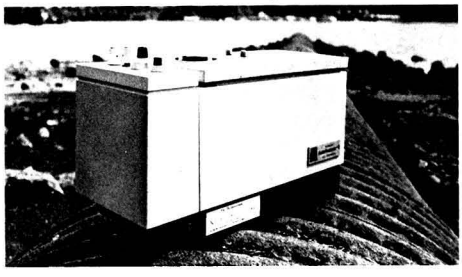

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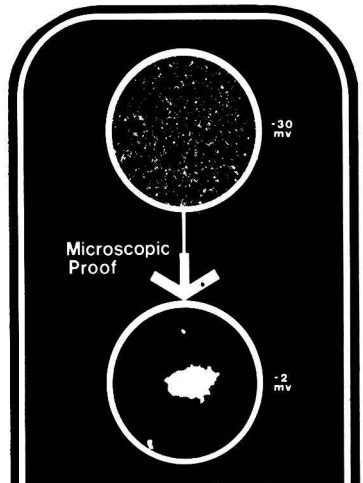

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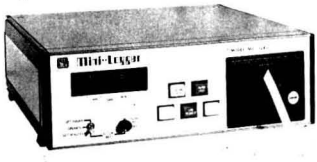

Sequential event recorder
The recorder is able to monitor up to 60 alarm signals emanating from dry contacts, series string contacts, or voltage. DATAcap **103**

Fuel oil viscometer
The viscometer increases burner efficiency and contributes to compliance with mandatory emission requirements. The unit can withstand vibration, temperatures to 300 °F, and pressures to 200 psi. Output is a 4–20 mA signal, proportional to viscosity. Brookfield Engineering Laboratories **104**

Stack sampling train
The emission-parameter-analyzer stack-sampling train permits the user to sample industrial and utility gas streams at isokinetic rates both accurately and simply, states the manufacturer. The system consists of a control unit, sample unit, and pitobe (probe) assembly. Andersen Samplers **105**

Sample fraction collector
This new accessory to the company's liquid chromatographs permits the user to collect automatically selected fractions of samples for analysis. Hewlett-Packard **106**

Dew-point hygrometer
This industrial model, System 1200A, is portable and suitable for panel mounting. Measurements are absolute, and outputs are continuous. Typical span is 80 to −40 °F at an ambient temperature of 80 °F. It is designed for applications where continuous readout with good accuracy is required. General Eastern **107**

Dust collectors
Three different sizes of downdraft bench dust collectors for grinding, buffing, assembly, and packaging operations are nominally rated at 1600, 3200, and 4800 ft^3 of air per min with an air cleaning efficiency of 99+%. American Air Filter **108**

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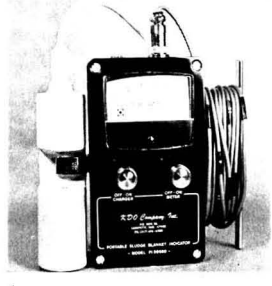

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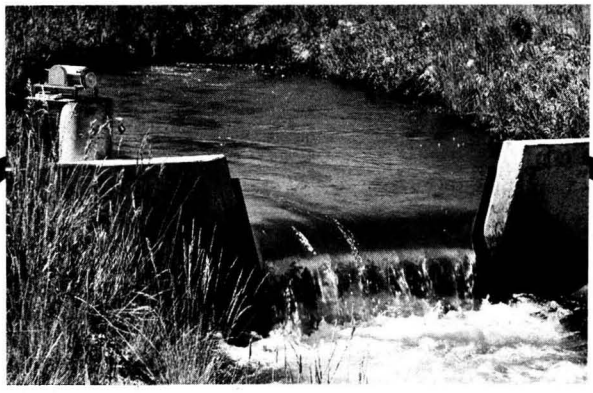

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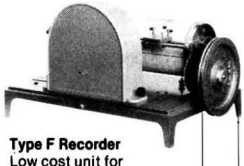

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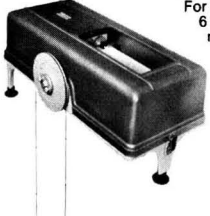

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High-density temperature monitors
The new thermocouple and RTD temperature monitors are capable of monitoring from 6–30 points. The units provide independent alarm and shutdown functions and linear digital readout and incorporate three-channel plug-in modules to provide high-density packaging. Rochester Instrument Systems **121**

Two-way, three-way solenoid valves
The valves are designed for microprocessor applications, and have power levels of 0.02–1 W. They are designed to handle vacuum and low-pressure fluids, and gases of all types. Angar Scientific **122**

Rotary vacuum pump
The single-stage pump is suitable for industrial rough vacuum applications between 760 and 100 Torr. Busch **123**

Gas sensing system
The unit is of modular design, suitable for sensor location in hazardous areas with the modular channels located centrally. Each module is self-contained with its own power supply, meter readout, test facilities, dual alarms, fault circuit, and relay functions. Gasvu Instruments **124**

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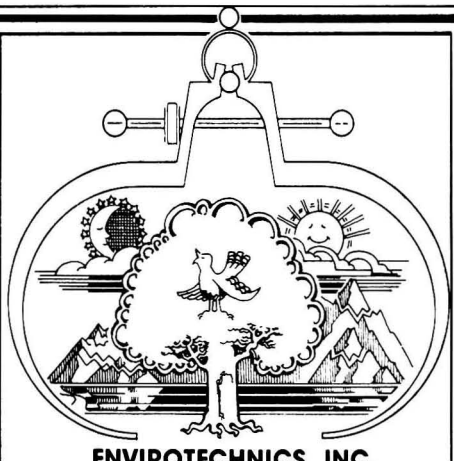
The unit aerodynamically sizes particles into nine fractions, has a flow rate of 2.8–28.3 L/min, and has a high capacity preimpactor that eliminates particle bouncing and reentrainment. The unit meets OSHA and EPA design requirements for respirable/nonrespirable particle fractionation. Gelman Sciences **125**

Liquid-level switches
The switches, mounted in compact bottle-type housings, are suitable for external installation on tanks and containers where access to the interior is not practical. Gems Sensors Division/Transamerica Delaval **126**

Data acquisition, handling system
This high-speed system is designed to complement the increased speed capabilities of current model gas chromatograph/mass spectrometers. Columbia Scientific Industries **127**

Organophosphonate test kit
The kit is designed to determine the phosphonate concentration in boilers and cooling towers. The test requires no acid digestion, boiling, or additional instrumentation. Results are obtained in minutes. Ecologic Instrument **128**

Ozone contactors
This modular ozone system is designed for cyanide destruction, and finds application in electroplating, mining, and other industries with effluents containing cyanide. It is fully automatic and has a capacity of 10–2000 gpm. U.S. Ozonair **129**



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CIRCLE 10 ON READER SERVICE CARD

ES&T LITERATURE

NO_x analyzer. Flyer sheet describes Model 235 NO/NO_x analyzer that works on principle of chemiluminescence. Applications for stack gas, diesel exhaust, and others. Scott Environmental Systems **151**

Particulate sampler. Bulletin No. 1178-244 lists Series 244 dichotomous samplers (virtual impactors) for sampling particulate matter. The technique was originally developed by EPA. Sierra Instruments, Inc. **152**

Inversion/wind detectors. Echosonde®, which detects air temperature inversions often responsible for pollution episodes and wind field characteristics, is described. Radian Corp. **153**

Problem solving. Brochure explains services in environmental problem-solving, and doing so with the least necessary expenditure of funds. Monsanto Environmental Services **154**

Dust control. Form GB describes TDC 1000 model, which combines cartridge filter technology with small capacity for intermittent dust collection. Torit Division, Donaldson Co., Inc. **155**

Water conservation/reuse. Bulletin 525-1 describes clarification techniques and corrosion/deposit control at coal preparation plants. Water conservation/reuse is an aim. Zimmite Corp. **156**

Noise protection. Brochure describes preassembled and portable acoustic personnel enclosures to protect people from unacceptable noise levels. Noise Control Products Inc. **157**

Chromatography. TLC brochure is a guide to products for thin-layer chromatography. Other data are included. Schleicher & Schuell, Inc. **158**

Exhausters. Catalog CBE-378 lists line of multi-stage centrifugal blowers and exhausters. Many applications: can range 100–25 000 inlet cfm; pressures to 18.5 psig; and vacuums to 16 in. Hg. Hoffman Air & Filtration Systems **159**

Fly ash collection. Brochure, "Air Pollution Control for Industrial Coal-Fired Boilers," is a case study of a precipitator installation. Fly ash collection and low power consumption are featured. United McGill Corp. **160**

Extractor. Bulletin G-1929-A1 features an oil solids extractor that separates oil-in-water emulsions and removes suspended solids through a separation medium. C-E Natco **161**

Air monitoring. Bulletin 07-0005M describes systems that monitor air for flammable and toxic components in enclosed spaces. Many different gases can be measured. Mine Safety Appliances Co. **162**

Permitting services. Brochure describes services for obtaining permits, preparing environmental impact statements, and other work for mining, power, and water resource projects. Harza Engineering Co. **163**

Chromatogram plotting. Publication 5953-1408 tells how to plot chromatograms automatically with a special computer terminal system. High resolution is provided. Hewlett-Packard **164**

Biofouling control. Data sheet describes potassium ferrate (K_2FeO_4), which may have applications for biofouling control, disinfection, and coagulation. Carus Chemical Co., Inc. **165**

Wastewater treatment. Publication B 568 describes wastewater treatment system using the basic oxidation with new design features, including a unique integral clarifier. LIGHTNIN® is the trade name. Mixing Equipment Co., Inc. **166**

***Companies interested in a listing** in this department should send their releases directly to Environmental Science & Technology. Attn: Literature, 1155 16th St., N.W., Washington, D.C. 20036*

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.

Sulfur determination. Bulletin No. AB-21 tells about a fast, simple method of determining the sulfur content of diesel and heating oils. Analysis time is less than 2 min/sample. Fisher Scientific Co. **168**

Water services. Brochure 1-32, "Creative Technology for Environmental Health," describes products/services for protecting drinking water, purifying products, treating wastewater, and many other tasks. Calgon Corp. **169**

Materials safety. Brochure describes a list of safety data for 370 materials found in many industrial plants. Prices for data lists are given ($195/set). General Electric **170**

Precipitator voltage. Bulletin describes AVCON 2000, an automatic voltage control system for electrostatic precipitators; it compensates for changes in gas/particulate conditions. Envirotech/Air Quality Control Group **171**

Chemical services. Catalog describes specialty chemicals and preparations for environmental and other work, sold in special, premeasured units for a particular job or experiment. Chem Service, Inc. **172**

Vacuum pumps. Bulletin VP-97 explains selection, applicability, and uses of Liquid Ring Vacuum Pumps. Croll-Reynolds Co., Inc. **173**

Fabric filters. Bulletin DCB-312B lists line of Dracco® fabric filter dust collectors, which work up to 550 °F. Wide selection of cloth media is available. Fuller Co. **174**

Bacteria cultures. Brochure tells how DBC Plus™ Dried Bacteria Cultures are being used in domestic wastewater facilities. Grease is eliminated, solids settle better, many other advantages. Flow Laboratories, Inc. **175**

Maintenance services. Brochure explains services for maintaining equipment on a comprehensive basis; could apply to wastewater treatment systems, also. B I F, a unit of General Signal **176**

Professionals in Chemistry 1978

. . . the fifth report in this series on the people who make up the chemical profession.

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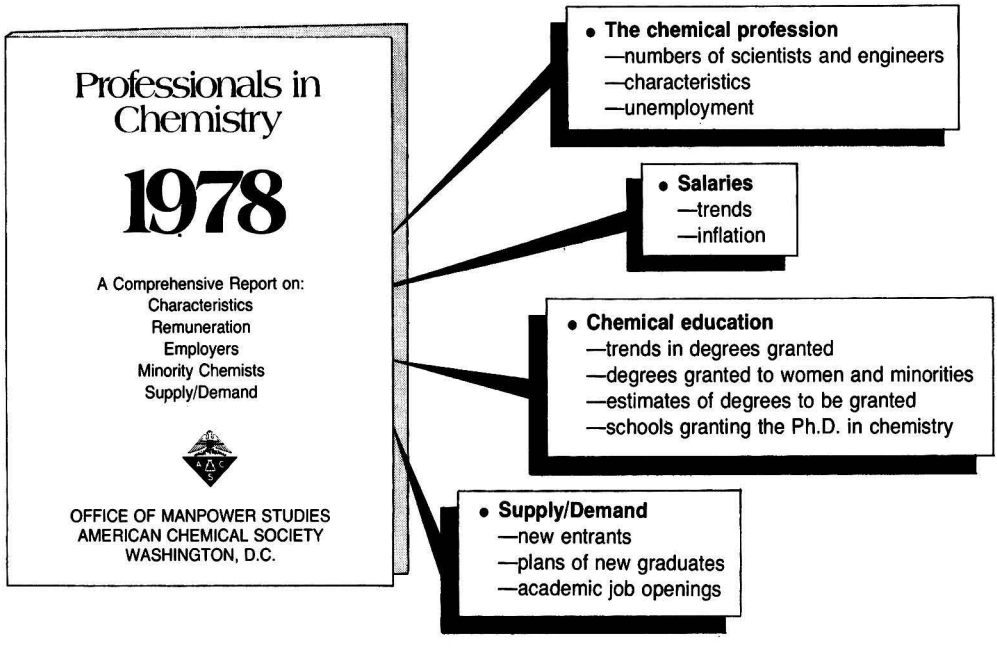

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PIC 1975 including a special report on salaries of women chemists and chemists' salaries compared with those of other professions
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Toxicology. *Toxicology Newsletter,* Vol. 5, No. 1, tells about automated equipment for analysis of toxics and gives information of general interest to toxicologists. Technicon Industrial Systems **177**

Analysis. Two catalogs list books on analysis by spectroscopy, chemical methods, chromatography, and many other techniques. Reference books and students' textbooks are listed, too. Heyden & Son Inc. **178**

Coal services. Brochure, "Upgrading Coal for the Future," covers preparation, washability, analysis of coal. Hazen Research, Inc. **179**

Primary standards. Literature release describes primary standards that can be prepared for 92 chemicals, many of which are environmental contaminants. Over 170 standards presented, as is material on permeation devices. Analytical Instrument Development, Inc. **180**

Combustion control. Brochure tells about benefits and features of Series 7150 Trim-Trol electronic combustion control that company says can achieve "substantial fuel cost savings." Cleveland Controls, Inc. **181**

Adsorbents. Technical Publication IE-254 describes laboratory column procedures for testing Amberlite® polymeric adsorbents. Loading, regeneration, and other technical matters are discussed. Rohm and Haas Co. **182**

Fabric filters. Booklet 610 describes Pulse-Jet fabric filter dust collectors with no moving parts. Bags are easily replaced, dust readily dislodged for future disposal. UOP Inc. **183**

Gas analysis. Product data sheet describes JUNIOR MODELS 510 and 610 gas analysis apparatus for methane, CO, hydrogen sulfide, sludge digestion gases, others. Burrell Corp. **184**

Fans and blowers. Brochure covers complete RT line of fans and blowers with capacities to 600 000 cfm, usable in temperatures up to 600 °F. Needs less horsepower; services many industries. Garden City Fan & Blower Co. **185**

Swimming pool cleaning. Brochure explains how diatomite filter powders are especially suitable for filtering and cleaning swimming pool water, and why they cost less. Witco Chemical **186**

Hydrocarbon detector (water). Bulletin announces a hydrocarbon detector for monitoring process streams, plant effluent, and boiler condensate. Can alarm as low as 5 ppm. AMSCOR **187**

Ion chromatography. Applications Note 15 explains use of ion chromatography to analyze combustion products of gasoline, fuel oil, diesel, sewage sludge, and coal for Clean Air Act compliance. Dionex Corp. **188**

Monitoring/control. Brochure tells how conductivity/resistivity measurements facilitate monitoring/control for boiler operation, rinse-water purity, power generation, and many other needs. Foxboro Analytical/Balsbaugh Center **189**

Inline flowmeters. Brochure covers fixed and retractable inline flowmeters and gives ranges, specifications, dimensions, ordering codes, and other pertinent information. Digitool **190**

Flocculants. Product Bulletin No. 1-300/78 describes SANDOLEC flocculants for wastewater treatment. They are polyelectrolytes and have many industrial/municipal applications. Sandoz Colors & Chemicals **191**

Clean Air Act. Monograph by Bradley Raffle explains prevention of significant deterioration, nonattainment, new sources, and many other aspects of the Clean Air Act. TRC **192**

Heated hoses. Booklet tells why heated hoses are needed, for example, to sample gases, transfer chemicals, dispose of wastes, and perform other tasks. Importance of thermal insulation is stressed. Technical Heaters, Inc. **193**

Flowmeters. Brochure describes pulse-jet top-access fabric filters with efficient bag cleaning. Engineering services with turn-key capabilities are also set forth. Johnson-March Corp. **194**

Filtration. Plate and frame filtration can help to clean water to sterilization, if necessary, collect valuable solids, or simply clean water. Particles to 0.1 μm can be collected, brochure says. Star Systems Filtration Division **195**

Low-flow estimation. Important to estimate pollutant drainage. Method applicable to other areas. Bulletin 117. Publications Sales, Geological Survey of Alabama, P.O. Drawer O, University, AL 35486 (write direct).

Mined land recovery. Film: "New Life for Ruined Land: Expanding the Frontiers of Environmental Research." Office of Public Affairs, Argonne National Laboratory, Argonne, IL 60439 (write direct).

Ozone disinfection. "Effect of Particulates on Ozone Disinfection of Bacteria and Viruses in Water," by Otis J. Sproul, et al., EPA-600/2-79-089. U.S. EPA, Municipal Environmental Research Laboratory, P.O. Box 19069, Cincinnati, OH 45219 (write direct).

Oil spill cleanup. How it was done off Prince Edward Island, Canada. EPS 3-EC-79-5. Publications Coordinator, Environmental Impact Control Directorate, Dept. of Environment, Ottawa, Ontario K1A OC8, Canada (write direct).

Residential solar energy. Stresses heating/hot water. Many reports on performance. U.S. Dept. of Energy, Technical Information Center, P.O. Box 62, Oak Ridge, TN 37830 (write direct).

Swedish environment. "Environmental Policies and Problems in Sweden," by Valfrid Paulsson, director-general of Swedish Environment Protection Board. FS 58. Swedish Information Services, 825 Third Ave., New York, NY 10022 (write direct).

Clean Air Act and RCRA. Two booklets explain each act and company policy. Corporate Communications, Union Carbide Corp., 270 Park Ave., New York, NY 10017 (write direct).

Waste treatment. Film, "An Investment to Protect," tells how Hinsdale, IL solved wastewater treatment plant problems and brought its plant up to expectations. John T. Rhett, U.S. EPA, Washington, DC 20460 (write direct).

Plutonium. "Plutonium-239 and Americium-241 Uptake by Plants from Soil," EPA-600/3-79-026. Environmental Monitoring and Support Laboratory, U.S. EPA, P.O. Box 15027, Las Vegas, NV 89114 (write direct).

Uranium determination. "Radiometric Method for the Determination of Uranium in Water," EPA-600/7-79-093. Environmental Monitoring and Support Laboratory, U.S. EPA, P.O. Box 15027, Las Vegas, NV 89114 (write direct).

ES&T BOOKS

The Brain: The Last Frontier. Richard M. Restak. 418 pages. Doubleday & Company, Inc., 245 Park Ave., New York, NY 10017. 1979. $12, hard cover.

This book is a compendium of current knowledge of the brain—how it works and how it is influenced by nutrition, environment, heredity, and drugs. The author chronicles animal studies, human data on malnutrition and its effect on brain size and intelligence, and how possibly inheritable brain central-processing activities may underlie heart diseases and some cancers, which also have environmental elements.

Nuclear Disaster in the Urals. Zhores A. Medvedev. vii + 214 pages. W. W. Norton & Co., Inc., 500 Fifth Ave., New York, NY 10036. 1979. $12.95, hard cover.

Did an atomic disaster, involving radioactive waste, occur in the southern Urals in late 1957? One leading British authority says, "No," but the author offers much documentation that suggests that an accident may, indeed, have taken place. This documentation includes accounts by people who were in the area at the time, as well as information gleaned from "sanitized" scientific papers on the subject. The author himself is in exile from the U.S.S.R. and is now living in England.

Handbook of Sludge-Handling Processes: Cost and Performance. Gordon L. Culp. x + 228 pages. Garland STPM Press, 545 Madison Ave., New York, NY 10022. 1979. $22.50, hard cover.

This book presents a single, comprehensive compilation of data on performance, capital costs, operation/maintenance costs, and energy needs for sludge processing units. Most, if not all, aspects of sludge handling are covered. Many alternatives are considered. This volume is part of the Garland Water Management Series.

Aerosol Measurement. Dale A. Lundgren et al. xxiv + 716 pages. University Presses of Florida, 15 N.W. 15th St., Gainesville, FL 32603. 1979. $45, hard cover.

Here, there is explained how to classify aerosols and analyze them. Origin and behavior of aerosols are considered, as well as numerous methods of measurement. Understanding of aerosols is extremely important to the knowledge and control of air pollution.

N-Nitrosamines. Jean-Pierre Anselme, Ed. x + 204 pages. Marketing Manager, Books Dept., American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. 1979. $22.50, hard cover.

N-Nitrosamines. Hardly a household word. But these compounds are suspected of being potent carcinogens and, indeed, have often come out positive on mutagenicity tests. They are produced in many ways, but a principal way is through nitrite reactions in food. Their chemistry, reactivity, and other aspects are considered in this book, which is No. 101 of the ACS Symposium Series.

The Passive Solar Energy Book: Expanded Professional Edition. Edward Mazria. xiii + 687 pages. Rodale Press, Inc., Organic Park, Emmaus, PA 18049. 1979. $24.95, professional hard cover; $12.95, hard cover; $10.95, paper.

The house itself and its immediate surroundings can themselves be "collectors" and utilizers of solar energy. But in order to achieve that desirable aim, one must design the house, and orient it to its surroundings, in certain ways. This book explains how to do these things in the most rational way and provides much technical data and comprehensibly worded, detailed how-to-do-it instructions and recommendations.

A Perspective of Environmental Pollution. M. W. Holdgate. x + 278 pages. Cambridge University Press, 32 East 57th St., New York, NY 10022. 1979. $35, hard cover.

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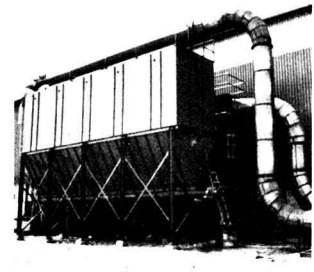

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This book explains how a given material becomes a pollutant. It describes pollutant pathways and principal environmental changes that these pollutants could cause. Other pollution aspects are considered, but perhaps the main thesis is that if important prevention measures are taken now, on a worldwide basis, then pollution need not be a threat to the future of mankind.

Environmental Impact Assessment: Principles and Applications. Paul A. Erickson. xiv + 395 pages. Academic Press, 111 Fifth Ave., New York, NY 10003. 1979. $26, hard cover.

This book explains how to assess the impacts needed in preparation of impact assessments, as required by NEPA. That would include physical environment, social, institutional, and many other impacts. The structure and function of the environmental impact assessment itself are discussed in detail.

The Solar Decision Book: A Guide for Heating Your Home with Solar Energy. Richard H. Montgomery, Jim Budnick. 283 pages. John Wiley & Sons, 605 Third Ave., New York, NY 10016. 1979. $12.95, paper.

This book tells how to do it, from negotiating an intelligent loan and pricing the job, to full installation of the system. Energy storage is also covered. How to determine what components are needed and what system size should be used are topics of discussion. Technical and numerical data are also presented.

Proceedings of the Water Reuse Symposium. 3 vols., 2400 pages, total. AWWA Research Foundation, 6666 West Quincy Ave., Denver, CO 80235. 1979. $15/set.

The symposium was held in Washington, DC, in March. It covered water supply augmentation, industrial recycling/reuse, aquaculture, wetlands, municipal and agricultural reuse, health/quality considerations, and many other similar and related topics.

Energy Technology VI: Achievements in Perspective. 1168 pages. Government Institutes, Inc., P.O. Box 5918, Washington, DC 20014. 1979. $38.

This volume contains 112 papers presented at the 6th Energy Technology Conference and Exposition and was edited by Richard F. Hill. It covers anthracite, environmental problems, fusion, "gasohol," nuclear, oil shale, and many other subjects involved in and closely related to present and future energy sources.

Liquid Filtration. Periodical publications in three units. The McIlvaine Company, 2970 Maria Avenue, Northbrook, IL 60062. All three units, $390/year.

This series goes exhaustively into liquid filters. There are descriptions of filter types, properties and uses, specifications with photos, industry data and applications, and much other important and pertinent information.

A Manual for the Use of SBA's Pollution Control Financing Guarantees. James H. McCall, Robert P. Feyer. 112 pages. Council of Pollution Control Financing Agencies, 10960 Wilshire Blvd., Suite 1806, Los Angeles, CA 90024. 1979. $15, paper.

This manual tells how a creditworthy small business can obtain funds for pollution control, on much the same advantageous basis that major national corporations can. Small Business Administration (SBA) guarantees are involved, and rates can average 7%. In some cases, tax-exempt industrial revenue bonds can be issued. Repayment averages 20 years. Projects costing $75 000–5 million have been so financed.

Hazardous Waste Report. Periodical. Aspen Systems Corp., 20010 Century Blvd., Germantown, MD 20767. $194/year; special rates may be available.

This report will cover enforcement, spill and hazard areas, litigation, Washington news, state news, industry case histories, and many other matters of which any industry affected by hazardous waste problems should be cognizant.

Municipal Sludge Compost Design. 220 pages. Information Transfer, Inc., 9300 Columbia Blvd., Silver Spring, MD 20910. 1979. $25.

This work covers compost technology, material handling equipment, federal rulings and guidelines, compost facility design, pretreatment requirements, and other topics pertinent to this composting effort.

Estimating the Hazards of Chemical Substances to Aquatic Life. STP 657. 283 pages. ASTM Sales Service Dept., 1916 Race St., Philadelphia, PA 19103. 1979. $19.50.

This work has, among its other aims, the objective of helping companies

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The Effect of Nitric Oxide Emissions on Photochemical Smog. W. B. Innes. 314 pages. Purad Inc., 724 Kilbourne Dr., Upland, CA 91786. 1979. $12.

The author notes that NO_x, in fact, helps to reduce photochemical smog and takes issue with A. J. Haagen-Smit that NO_x increase this smog. He suggests that rational, minimal NO_x controls, together with "common sense" hydrocarbon control measures, say, for cars, would actually do more to minimize smog than would an expensive, fuel-consumptive NO_x control installation.

The Beaches Are Moving: The Drowning of America's Shoreline. Wallace Kaufman, Orrin Pilkey. 336 pages. Doubleday and Co., Inc., 245 Park Ave., New York, NY 10017. 1979. $10.95, hard cover.

Beaches erode and wash out from under houses and hotels. The authors propose that this is not caused necessarily by freak storms or "acts of God," but simply that the sea level has long been rising. But the urge to live right near the beach does not take these facts into account. How to choose a safe site and to tell dangerous from safe development are two of the topics discussed.

Advances in Photochemistry, Vol. III. James N. Pitts, Jr. et al. xii + 538 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1979. $35.95, hard cover.

Many aspects of photochemistry are covered here. However, there are some of great environmental importance. These include behavior of the hydroxyl radical in air, under sunlight, in the presence of organic compounds.

Environmental Health Criteria 8: Sulfur Oxides and Suspended Particulate Matter. 108 pages. WHO Publications Centre USA, 49 Sheridan Ave., Albany, NY 12210. 1979. About $6, paper.

The most important route of human exposure to sulfur compounds is through inhalation, on which this book concentrates. Most of this sulfur comes from combustion of fossil fuels. This work considers the matter of human exposure, and looks into biological action of these pollutants.

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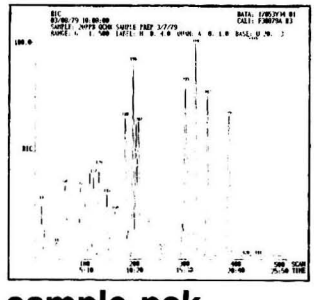

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Write: Jan Connery, ERCO, Inc., 185 Alewife Brook Parkway, Cambridge, Mass. 02138

September 19–21 Cincinnati, Ohio
National Symposium on Wastewater Aerosols and Disease. U.S. Environmental Protection Agency
Write: Virginia Hathaway, JACA Corp., 550 Pinetown Rd., Fort Washington, Pa. 19034

September 23–26 Las Vegas, Nev.
The 6th Annual National American Society for Quality Control: Energy Division Conference. The American Society for Quality Control
Write: F. B. Hyland, Westinghouse, P.O. Box 1313, Pensacola, Fla. 32596

September 23–26 Los Angeles, Calif.
1979 Mining Convention. The American Mining Congress
Write: American Mining Congress, 1100 Ring Building, Washington, D.C. 20036

September 23–26 Detroit, Mich.
Toxic Substances in the Human Food Chain: Implications for Public Health Practice. The Michigan Public Health Association
Write: University of Michigan Extension Services, Conferences & Institutes, 412 Maryland St., Ann Arbor, Mich. 48109

September 23–26 Chicago, Ill.
The 9th North American Thermal Analysis Society Meeting. The North American Thermal Analysis Society
Write: Barbara Fabricant, Glass Thermochemistry R&D, Owens-Corning Fiberglas Technical Center, P.O. Box 415, Granville, Ohio 43023

September 24–25 Chicago, Ill.
Fuels Use Planning: New Strategies. The Energy Bureau Inc.
Write: Robert Nash, Executive Director, The Energy Bureau Inc., 41 East 42nd St., New York, N.Y. 10017

September 24–28 Chicago, Ill.
Design, Installation and Operation Criteria for Solar Energy Systems Symposium. The Institute of Gas Technology
Write: Kathy Fisher, IGT, 3424 South State St., Chicago, Ill. 60616

September 24–28 Las Vegas, Nev.
The 15th American Water Resources Conference. The American Water Resources Association
Write: The American Water Resources Association, St. Anthony Falls Hydraulics Laboratory, Mississippi River at Third Ave., S.E., Minneapolis, Minn. 55414

September 27–28 Denver, Colo.
Health Effects of Air Pollution. American Medical Association and the Colorado Medical Society
Write: American Medical Association, Department of Environmental, Public and Occupational Health, 535 N. Dearborn St., Chicago, Ill. 60610

September 28 Chicago, Ill.
Air Quality Conference. The Illinois–Indiana Bi-State Commission
Write: Jeanne Millin, Projects Coordinator, Illinois–Indiana Bi-State Commission, One East Wacker Drive, Chicago, Ill. 60601

October 1–3 Washington, D.C.
Waterpower '79. The International Conference on Small Scale Hydropower. The U.S. Army Corps of Engineers and the U.S. Department of Energy
Write: Waterpower '79, 1129 20th St., N.W., Suite No. 511, Washington, D.C. 20036

October 2–4 Columbus, Ohio
4th International Symposium on Polynuclear Aromatic Hydrocarbons. Battelle's Columbus Laboratories
Write: Alf Bjorseth, Symposium Chairman, Battelle's Columbus Laboratories, 505 King Ave., Columbus, Ohio 43201

October 2–4 Manhattan, Kans.
An International Symposium on Grain Dust. The United States Dept. of Agriculture, the Grain Elevator and Processing Society, and the National Grain and Feed Association
Write: B. S. Miller, U.S. Grain Marketing Research Laboratory, 1515 College Ave., Manhattan, Kans. 66502

October 2–5 Syracuse, N.Y.
The 9th Northeast Regional Meeting of the American Chemical Society. The American Chemical Society
Write: R. J. Conan, Jr., Dept. of Chemistry, LeMoyne College, Syracuse, N.Y. 13214

October 3–5 Wilmington, Del.
Stormwater Management Alternatives: A National Conference. The University of Delaware Water Resources Center and the U.S. Dept. of Interior Office of Water Research and Technology
Write: Conference Administration, University of Delaware, Water Resources Center, 42 E. Delaware Ave., Newark, Del. 19711

October 3–5 Kansas City, Mo.
The 4th National Passive Solar Conference. The International Solar Energy Society
Write: The 4th National Passive Solar Conference, P.O. Box 1643, Jefferson City, Mo. 65102

October 3–5 Cherry Hill, N.J.
The American Association of Textile Chemists and Colorists 1979 National Technical Conference. The American Association of Textile Chemists and Colorists (AATCC)
Energy and environmental issues will be discussed. *Write:* AATCC, P.O. Box 12215, Research Triangle Park, N.C. 27709

October 3–5 Gatlinburg, Tenn.
Biotechnology in Energy Production and Conservation. The U.S. Department of Energy and the Oak Ridge National Laboratory
Write: Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830

October 4 Boston, Mass.
Hazardous Waste Management: Requirements of the Resource Conservation and Recovery Act. New England Research, Inc.
Write: New England Research, Inc., 15 Sagamore Rd., Worcester, Mass. 01605

October 7–10 Daytona Beach, Fla.
Advances in Particle Sampling and Measurement. The Southern Research Institute
Write: Kenneth Cushing, Southern Research Institute, 2000 Ninth Ave., South, Birmingham, Ala. 35205

October 7–11 Charlotte, N.C.
1979 Joint Power Generation Conference. The American Society of Mechanical Engineers
Write: The American Society of Mechanical Engineers, United Engineering Center, 345 East 47th St., New York, N.Y. 10017

(continued on page 1164)

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October 9–11 Gaithersburg, Md.
The 4th Annual Conference on Materials for Coal Conversion and Utilization. The National Bureau of Standards
Write: Kathy Stang, Room B348, Materials Building, NBS, Washington, D.C. 20234

October 9–11 Gatlinburg, Tenn.
The 23rd Oak Ridge National Laboratory Conference on Analytical Chemistry in Energy Technology. The Oak Ridge National Laboratory
Write: W. S. Lyon, Technical Program Chairman, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830

October 10–12 New Orleans, La.
The 1979 Marine Technology Society Exhibition and International Conference. The Marine Technology Society
Write: The Marine Technology Society, Headquarters Suite 412, 1730 M St., N.W., Washington, D.C. 20036

October 11–13 Monterey, Calif.
The 23rd Annual Western Occupational Health Conference. The American Occupational Medical Association
Write: B. H. Bravinder, Executive Secretary, P.O. Box 201, Alamo, Calif. 94507

October 15–17 Jekyll Island, Ga.
The 3rd International Symposium on Aquatic Pollutants. The American Institute of Biological Sciences and the U.S. EPA
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Control, Operation, and Management of Biological Wastewater Treatment Plants. Vanderbilt University
Fee: $395. *Write:* Vanderbilt University, Box 6222, Station B, Nashville, Tenn. 37235

September 18–20 New Orleans, La.
Wastewater Treatment Facilities for Small Communities. The U.S. EPA
No fee. *Write:* U.S. EPA, c/o Enviro Control, Inc., P.O. Box 828, Rockville, Md. 20851

September 18–21 Minneapolis, Minn.
Control of Particulate Emissions (Lecture course). U.S. EPA.
Fee: $88. *Write:* Registrar, Air Pollution Training Institute, MD-20, U.S. EPA, Environmental Research Center, Research Triangle Park, N.C. 27711

September 20–21 New York, N.Y.
Innovative and Alternative Technology Assessment. U.S. EPA
No fee. *Write:* U.S. EPA, c/o JACA Corporation, 550 Pinetown Rd., Ft. Washington, Pa. 19034

September 24–28 Cincinnati, Ohio
Liquid Chromatography: Separation Plus Spectroscopy. The Finnigan Institute
Fee: $625. *Write:* Ann Woolley, Finnigan Institute, 11750 Chesterdale Road, Bldg. No. 5, Cincinnati, Ohio 45246

October 1–3 Washington, D.C.
Preparation of Environmental Impact Statements. The George Washington University
Fee: $435. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

October 3–5 Albany, N.Y.
Air Management. Airtechnical Enterprises, Inc.
Fee: $345. *Write:* Thomas Cutter, Seminar Director, Airtechnical Enterprises, Inc., 29-28 41st Ave., Long Island City, N.Y. 11101

October 10–12 Washington, D.C.
Air Pollution Control Equipment: Operation and Maintenance. The George Washington University
Fee: $430. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

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October 11-12 Atlanta, Ga.
Environmental Laws & Regulations (Introductory course). Government Institutes, Inc.

Fee: $375. *Write:* Government Institutes, 4733 Bethesda Ave., Suite No. 806, Washington, D.C. 20014

October 15-19 Boston, Mass.
Industrial Hygiene Workshop, Evaluation and Control of Occupational Hazards: Basic Skills. Harvard University

Fee: $500. *Write:* Short Course Coordinator, Dept. of Environmental Health Sciences, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115

October 16-17 St. Louis, Mo.
The 2nd AES Coatings for Solar Collectors Symposium. The American Electroplaters' Society, Inc.

Fee: $150 (members); $185 (nonmembers). *Write:* Mary Lou Dowdell, Manager, Meetings/Conferences, AES Headquarters, 1201 Louisiana Ave., Winter Park, Fla. 32789

October 17-19 Washington, D.C.
Wastewater Engineering. The George Washington University, the Illinois Institute of Technology, and Vanderbilt University

Fee: $435. *Write:* Continuing Engineering Education, George Washington University, Washington, D.C. 20052

Call for Papers

October 1 deadline
Combined Municipal-Industrial Wastewater Treatment. The U.S. EPA and the University of Texas at Dallas

Conference will be held March 25-27, 1980, at Dallas, Tex. *Write:* Aharon Netzer, University of Texas at Dallas, P.O. Box 688, Mail Station BE 22, Richardson, Tex. 75080

October 1 deadline
The 34th Annual Technical Conference of the American Society for Quality Control. The American Society for Quality Control

Conference will be held May 19-21, 1980, in Atlanta, Ga. *Write:* Maxwell Jeane, Route No. 1, Box 105, Randall Court, White Plains, Md. 20695

October 15 deadline
26th Annual Technical Meeting of the Institute of Environmental Sciences. Institute of Environmental Sciences

Conference will be held May 11-14, 1980, in Philadelphia, Pa. *Write:* Henry Caruso, Westinghouse Electric Corporation, Box 746, Mail Stop 504, Baltimore, Md. 21203

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- ☐ 3. 100 - 299
- ☐ 4. 300 - 499
- ☐ 5. 500 - 999
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- ☐ 7. Over 3000

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- ☐ B. Water pollution only
- ☐ C. Waste treatment only
- ☐ D. Air & Water pollution
- ☐ E. Air & Waste treatment
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- ☐ E. Food/Beverages
- ☐ F. Textile/Fiber
- ☐ G. Pulp/Paper/Wood
- ☐ H. Soaps/Cleaners
- ☐ I. Paint/Coating/Ink
- ☐ J. Agrichemicals
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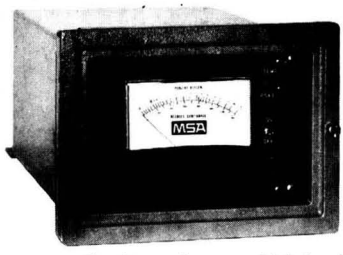
MSA INSTRUMENTS in the NEWS
COMBUSTION CONTROL • HEALTH & SAFETY • ENVIRONMENTAL • PROCESS

Accurate combustion control with MSA Oxygen Analyzer helps industry save scarce fuel.

Since its introduction in 1975, the Model 803 Oxygen Analyzer from MSA has received a warm welcome from combustion engineers across industry. Wherever fuel is burned for process heat, power generation or manufacturing, fine tuning of excess air in the combustion process pays big dividends. It used to be difficult to get reliable readings in the hot, dirty conditions in the stack. But the Model 803 O_2 Analyzer is changing all that.



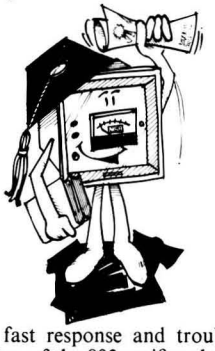
Located right on the stack, the Model 803 gives you the shortest possible sampling line. It operates hot so that gases are kept above their dewpoint. That minimizes plugging problems and increases time on line without shutdown. The analyzer measures oxygen directly—not just an effect of oxygen. So it produces a high-level signal. And its sensitivity holds through the full 0.1% to 21% O_2 range.

Many users have commented on the 803's speed of response when furnace operating conditions vary. Prompt corrective action saves them fuel and avoids pollution incidents.

MSA Oxygen Analyzer goes to "energy college."

The engineering department of a southern college conducts seminars to help industry improve their boiler operating efficiency. During the lecture portion, the Model 803 Oxygen Analyzer demonstrates the theory of excess air control; then the professor takes the group of boiler operators and superintendents to a nearby industrial plant to observe this combustion control theory in operation.

The class analyzes the combustion gases from the boiler with the Model 803 and correlates the analysis to Orsat tests. Conditions are deliberately varied, and effect on excess air and efficiency noted.



The fast response and trouble-free operation of the 803 verifies classroom data and confirms how simple it is to continuously maintain the correct excess air ratio.

Flue gas analysis goes portable.

The popular Model 803 is now also available as the 803-P Portable O_2 Analyzer. The 20-pound unit is complete in a single case with handle. It offers the same high levels of accuracy, measuring O_2 from 0.1% to 21%. The logarithmic scale provides highest accuracy at the lowest concentration levels.

While measuring flue gas excess oxygen is a major application, inert gas generators, heat-treating atmospheres and other combustion processes can all benefit from its use. You just plug it in at the test location, and within 20 minutes you're ready for accurate analysis of combustion oxygen level. Adjustments in ratios are recorded in seconds for fast correction of fuel/air imbalances.

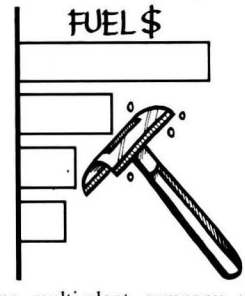
How can we help you?

MSA has experienced instrumentation engineers in your area who can review your needs and make specific proposals for your plant. They can also provide details on other MSA instruments for stack emission monitoring, health and safety analysis systems and air quality monitoring. Check the Yellow Pages for the nearest MSA office or write MSA Instrument Division, 600 Penn Center Blvd., Pittsburgh, Pa. 15235.

Multi-plant air analysis shows how to shave fuel costs.

In the dim, dark past when fuel was cheaper than controls, boiler operators didn't mind losing a little heat in the form of excess air. It was heated and then carried its Btu's right out the stack, but it didn't bother the burning rate or the operation.

Now, that "little heat" can add up to a loss of thousands of dollars *every month*. More and more industrial boiler operators are turning to oxygen monitoring and control as a cost-efficient way to reduce fuel consumption.



One multi-plant company studied the effect of increasing boiler efficiency from 1% to 5% for four classes of boilers. The figures showed, for example, that a 2% improvement for a 100,000-lb boiler would offer savings of $3,000 *per month* when fuel was 26¢ a gallon. At that rate, the cost of controls could be paid off in a matter of months.

Today, saving fuel is not just a matter of economics—it can be the difference between operating or shutting down in cold weather.

As a bonus, efficient combustion processes are less likely to create air pollution problems from the stack.

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