

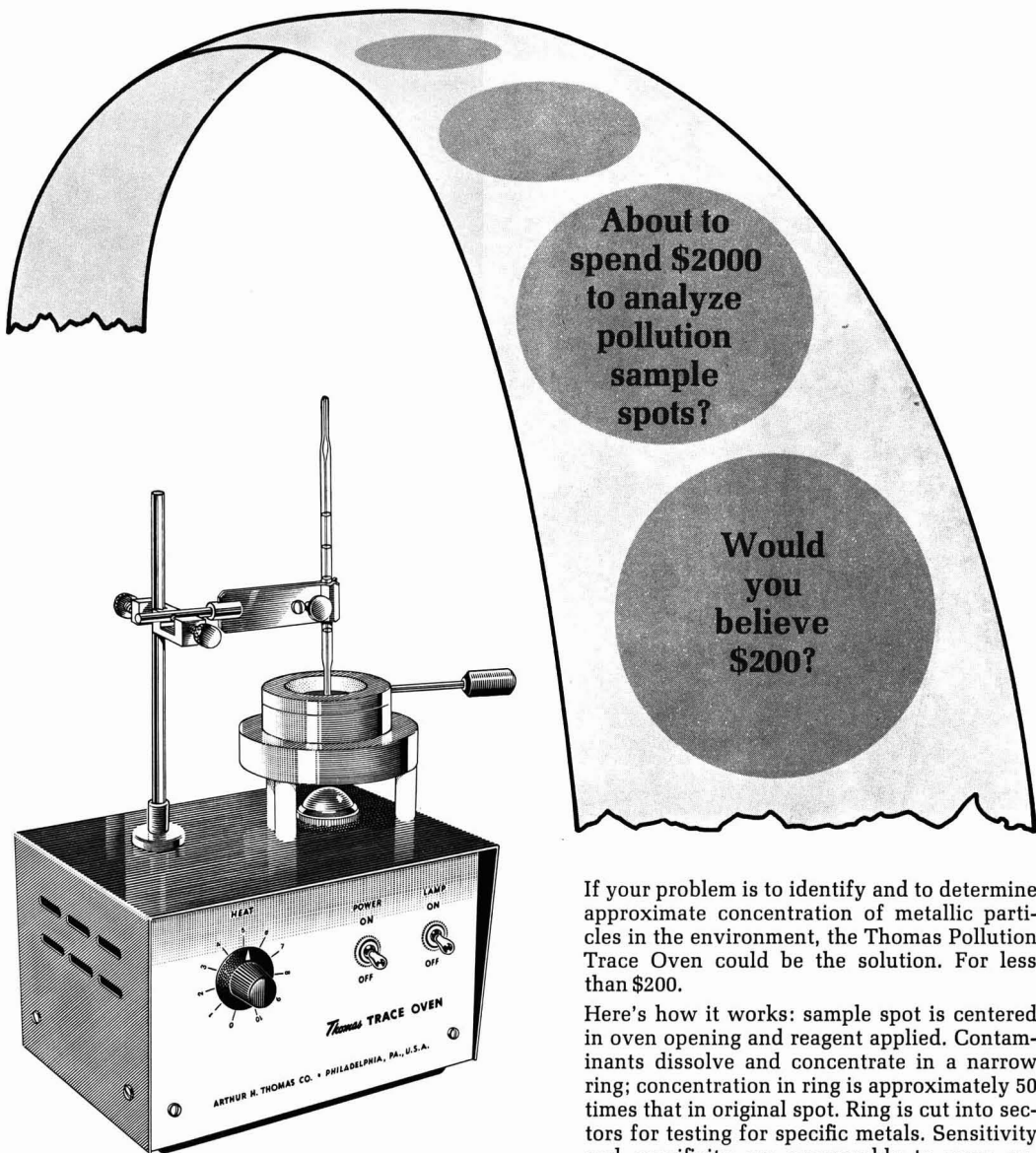
# Environmental

Science & Technology

APRIL 1972



Wholesaling environmental services 324



The TRACE OVEN methods for inorganic pollutants have been developed at Louisiana State University by Prof. P. W. West and his associates. These methods have been described by Prof. West in "Air Pollution," Volume II, 2nd Edition (Academic Press, New York, 1968, A. C. Stern, Editor), pp. 147-185.

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## Current research

### Mathematical model for fate of pollutants in near-shore waters 331

W. J. Wnek and E. G. Fochtman

Predictive techniques are available for calculating the fate of water-borne pollutants such as sewage and industrial wastes in lakes. For example, the individual and combined pollution effects of three outfalls situated on the shoreline of Lake Michigan can be learned from such mathematical models. The models point out the concentration of pollutants in the near-shore water of the lake, for example, the concentration of BOD along the shoreline and 50 ft from the shore.

### Variations of sulfur isotope ratios in samples of water and air near Chicago 338

B. D. Holt, A. G. Engelkemeir, and A. Venters

Pollution in the vicinity of a large city can be assessed by measurement of  $^{34}\text{S}$  enrichments in environmental samples—atmospheric precipitation, rain, and groundwater systems. Data are shown for a suburban area of Chicago; the data are provided by mass spectrometric analysis.

### Photochemistry of atmospheric samples in Los Angeles 342

S. L. Kopczynski, W. A. Lonneman, F. D. Sutterfield, and P. E. Darley

Samples of polluted air from Los Angeles were collected in plastic bags, irradiated with sunlight, and subsequently analyzed for the components of photochemical smog. Excluding methane, the paraffins as a class showed one fifth the average reactivity (based on percentage consumption) of the olefins, and the aromatics, one half. The aromatics, however, accounted for the greatest yield of reacted carbon atoms in the atmospheric samples irradiated for 4 hr at full sunlight intensity.

### Critical evaluation of the Saltzman technique for $\text{NO}_2$ analysis in the 0–100 ppm range 348

D. H. Fine

The Saltzman technique has been critically reevaluated and modified so that it can be reliably used for the determination of  $\text{NO}_2$  in which about 95% of the sample is nitric oxide. The reproducibility of the method has been established to better than  $\pm 0.3\%$ .

### Properties of carbonate rocks related to $\text{SO}_2$ reactivity 350

R. H. Borgwardt and R. D. Harvey

One major factor in the development of a limestone-based process for control of  $\text{SO}_2$  emissions from stack gases depends on the wide variety of naturally occurring rocks—dolomites and limestone. The variation in reactivities can be explained by differences in the physical properties of the calcined products; 11 specimens were investigated for their reactivity with  $\text{SO}_2$ . Both pore size and particle size of the rocks were important parameters. Small pores result in high reaction rates, but if the particles are large, then the capacity is low.

### Analytical studies of simplified photochemical smog kinetics 360

M. Lipeles and N. Malmuth

Mathematical models are useful to simulate atmospheric rate processes which describe the formation and buildup of photochemical smog. A simplified system is described which includes sets of equations of considerably lower order than those accounting for the production of all intermediate species such as free radicals. By application of analytical techniques, results have been obtained which are difficult, if not virtually impossible, to obtain by numerical solutions.

## Communications

### Singlet $\text{O}_2$ production from photoexcited $\text{NO}_2$ 365

T. Frankiewicz and R. S. Berry

The role of singlet molecular oxygen may still be important to explain the production of photochemical smog. Mechanisms involving benzene, benzaldehyde, naphthalene and naphthalene derivatives seem relatively unimportant for smog formation, but another possible mechanism is noted for generating singlet molecular oxygen.

### Sunlight photochemistry of ferric nitrilotriacetate complexes 367

T. Trott, R. W. Henwood, and C. H. Langford

Accumulation of NTA in natural waters is limited because of the photodegradation of an iron-containing complex of the material. There is some evidence suggesting that this degradation reaction described here could be important to at least depths of 10 meters in typical natural water situations.

## Correspondence

### Uranium concentrations in surface air 368

B. Kalmon  
W. G. Myers

Attention is called to the matter in an earlier paper that all measurements are reported in mass concentration units whereas all data reported by the Piketon nuclear gaseous diffusion plant in Ohio are given in radioactivity concentration units. It is well known that conversion of radioactivity units to mass units requires knowledge of the isotopic composition of the sample.

Credits: 303, UPI; 309, 310, 314, Stan Miller; 317, Grumman Aerospace Corp.; 319, Stan Miller; 322 Westinghouse Electric Corp.; 326, 328, Maryland Environmental Service.  
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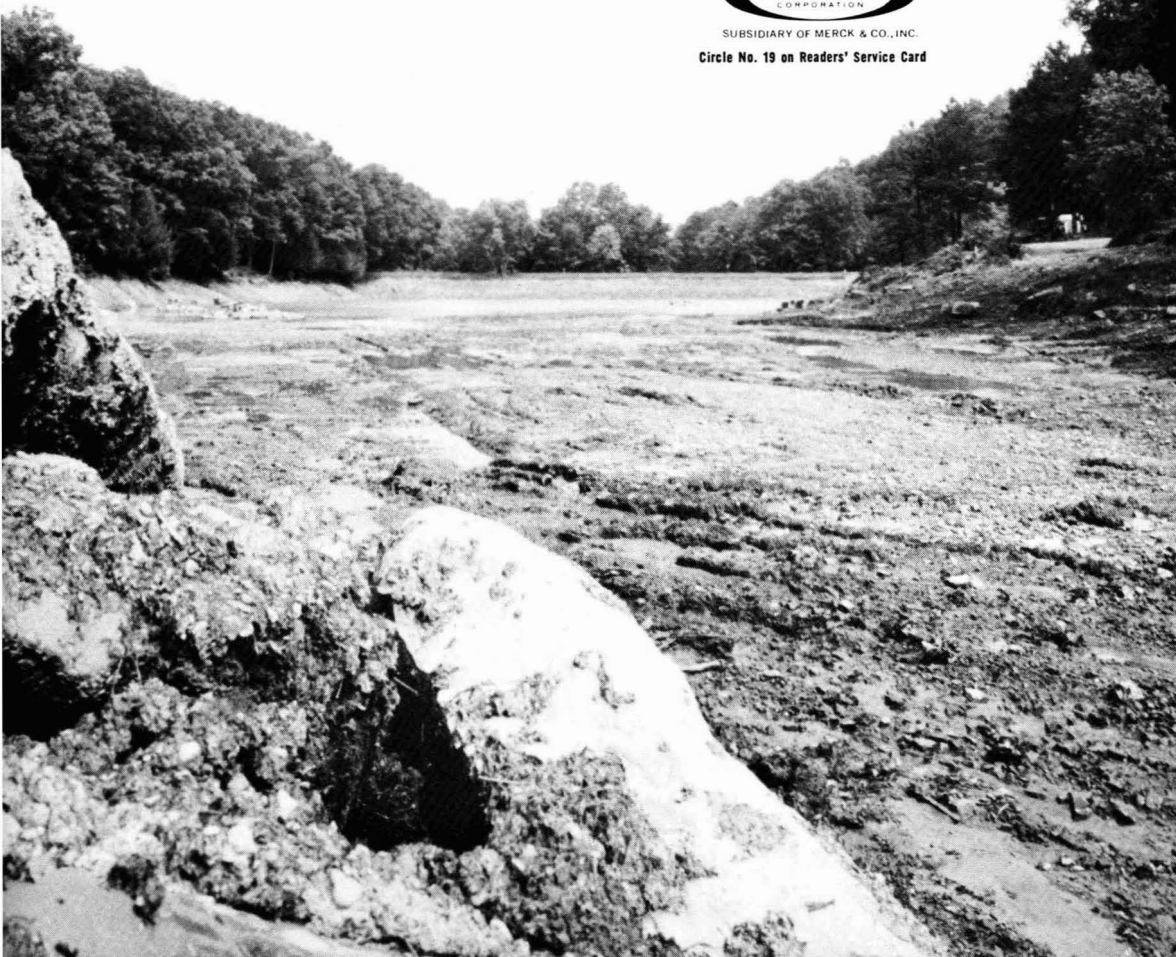
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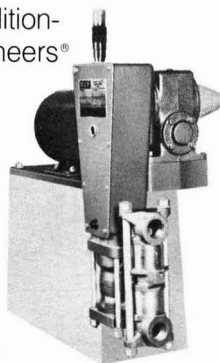
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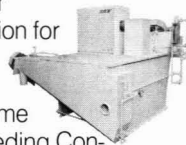
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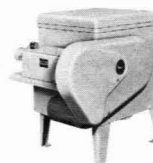
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# letters

## Detergent phosphate replacement

DEAR SIR:

In Richard Grundy's informative article, "Strategies for control of man-made eutrophication" (ES&T, December 1971, p 1184), an assumption is made regarding the cost of replacing sodium tripolyphosphate (STP) with NTA, relative to the cost of effluent treatment on a national basis for the removal of phosphate. The assumption is that treatment for phosphate removal would be lower in cost to the consumer-taxpayer than the cost of substituting NTA for STP in household detergent products. The increase in product material cost is noted to be 5 cents/lb.

Complete replacement of STP with NTA is not technically feasible. NTA, when formulated into a detergent composition as the total effective builder, produces an unstable product with respect to storage stability. To prevent caking and to provide a useful shelf life, it is necessary to use a mixture of

NTA and STP. The approximate ratio 30 parts of NTA to 20 parts of STP is commonly used.

Accordingly, the estimates of the relative costs of detergent phosphate replacement vs. total or partial phosphate removal have to be reexamined. With the use of NTA, approximately 40% of the amount of detergent phosphate normally embodied in the washing composition would still be used and would be subject to removal with its associated cost.

Hygienically safe, noncarbonate, nonphosphate, nonpolluting washing compositions, now under development, do show promise as useful replacements for phosphate detergent products. Colloidal silica is one such detergent builder. A silica-built composition is lower in material cost than a conventional phosphate-built composition—65 vs. 94 cents/lb.

The benefits of tertiary treatment for effective removal of phosphorus

are apparent, and an all-out effort to activate such treatment systems, where needed, should be made. However, the time factor in reaching this achievement is highly significant. With the time lag involved in funding, design, construction, and activation of plants, further deterioration of water quality in the interim period is virtually ensured.

Pending the use of adequate treatment systems, guarded regulation of the embodiment of nutrients in detergent products at the municipal, county, or state level is needed.

**Louis McDonald**  
*Pollution Abatement Foundation  
Altadena, Calif. 91001*

## Silicates in detergents

DEAR SIR:

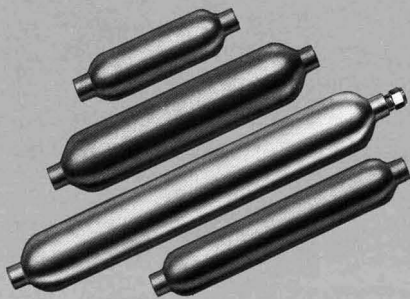
As a leading manufacturer of sodium silicate, we would like to comment on the article on control of eutrophication by Richard Grundy in the December 1971 issue of ES&T (p 1184).

Grundy's discussion of "phosphate

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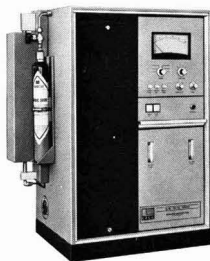
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substitutes" may create the impression that sodium metasilicate and other forms of sodium silicate are employed in low-phosphate and no-phosphate detergents as novel ingredients. The fact is that sodium silicate has been used in practically all the changing types of home laundry soaps and detergents for more than a century. A relatively low-alkali form of sodium silicate is to be preferred in household detergents and has traditionally been favored. It has an exceptionally long history of safety to human health and is generally regarded as ecologically innocuous.

The more strongly alkaline metasilicate has been used to some extent for at least 40 years, especially where available equipment is limited to processing of dry ingredients. A suitable dry form of low-alkali sodium silicate, called hydrous polysilicate, has only recently become commercially available.

Phosphate-free detergents do not necessarily contain any more sodium silicate, or a more alkaline form, than do phosphate detergents. Sodium silicate, which is safe in phosphate detergents, does not become "caustic" when the phosphate is omitted.

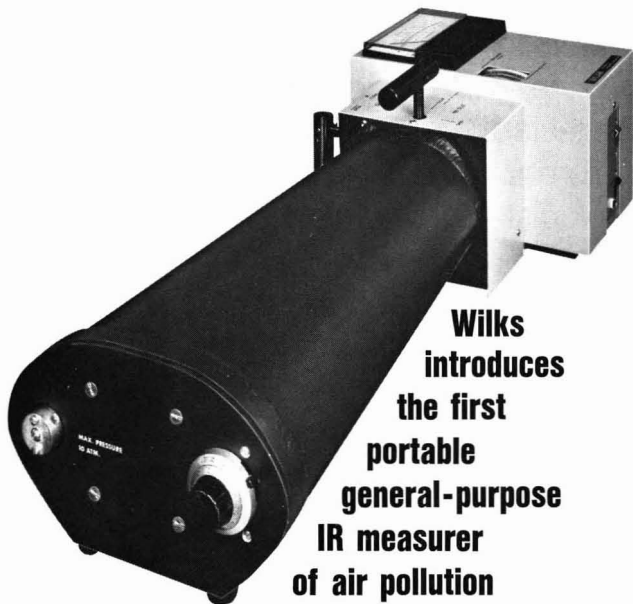
Alkalinity is not the only potential health hazard in detergents. Some detergent products bear warning labels but contain no alkaline ingredients whatsoever. Safety depends on the nature and amount of all of the ingredients. Consequently, both phosphate detergents and phosphate-free detergents can vary widely in potential health hazard. The Surgeon General has modified his original statement to stress this point. It is further demonstrated by the cautionary labeling requirements of the Food and Drug Administration under the Federal Hazardous Substances Act.

One of the principal reasons for including sodium silicate in laundry detergents, regardless of phosphate content, is its effectiveness as a corrosion inhibitor. The risk of corrosion to metals and to ceramic surfaces does not depend on alkalinity but on the ingredient employed. Similarly, sodium silicate prevents loss of fabric strength when compared to other washing solutions of equal alkalinity. A degree of alkalinity is indispensable to effective laundering.

We quite agree that massive alkalinity of laundry products could create a health hazard in the home, but this point has been unduly exploited in defense of phosphate. The Surgeon

*(Continued on p 302)*

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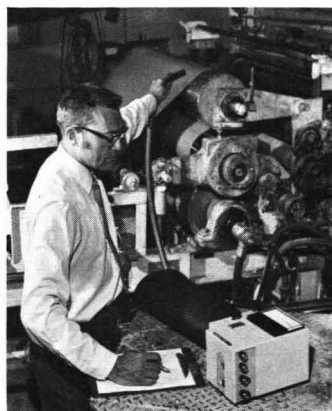
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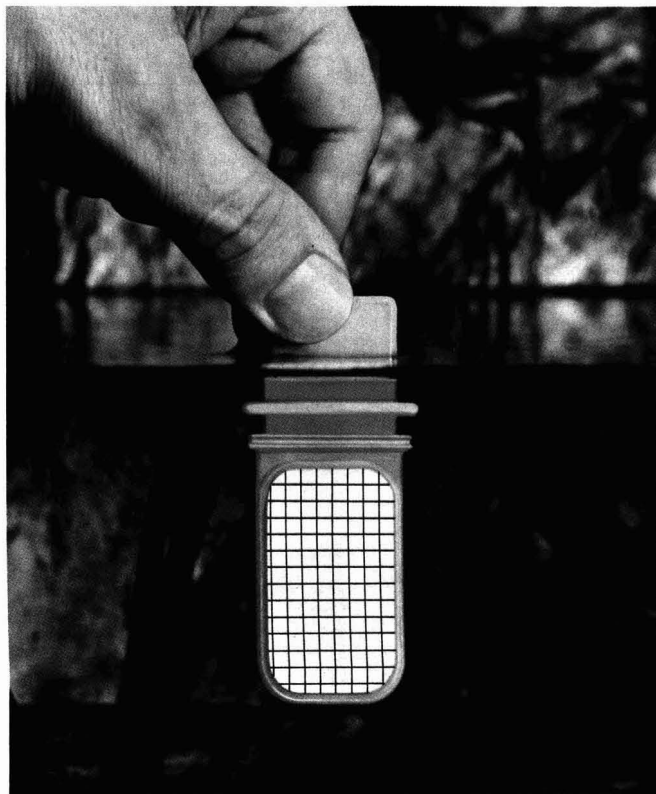
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General has stated that existing legislation provides the means of coping with the safety problem. And he has acknowledged that not all phosphate-free detergents are hazardous to health.

**Walter L. Schleyer**  
*Government and Industry Relations  
Manager  
Philadelphia Quartz Co.  
Philadelphia, PA 19106*

#### Environmental job opportunities

DEAR SIR:

I'm writing about the article, "Manpower for Environmental Protection," in the April 1971 issue of *Environmental Science & Technology* (p 314). This article presents the hypothesis that there will soon be a nationwide shortage of trained personnel in environmental technology. A splashy reprint of this article is currently being distributed by EPA.

A close examination of the article reveals that there is not one scintilla of evidence presented to support the above hypothesis. The article presents graphs and tables of past, present, and future manpower requirements without any support or backing whatsoever. Beyond that, it degenerates into a mere description of jobs performed by workers in this field. Thus it conveys the misleading impression that there will be great numbers of job openings in environmental technology, which tends to lure people into the field. This is exactly what happened in aerospace in the 50's and 60's, until the field was oversupplied with talent. Then the big bust came.

You can assure nationwide organization of engineers by continuing to publish articles about urgent future needs for them. The worst enemy of the working engineer is the technical society which works to assure an oversupply. However, the influence of such societies is waning, as many are being taken over by working engineers, and future engineers are learning the truth. There will come a day when you won't be able to publish an article like your "Manpower..." one at all, because no one will read it without laughing.

**Robert Bruce**  
*15 Johnstone Rd.  
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# environmental currents

## **WASHINGTON EPA: lead, secondary treatment, and turn-key**

On February 23, EPA Administrator William Ruckelshaus proposed regulations providing for general availability of one grade of lead-free and phosphorus-free gasoline by July 1, 1974, along with a phased reduction in the lead content of regular and premium gasolines. The 90-day hearing period for comments on this proposal expires next month. EPA's requirement of providing for secondary treatment of wastes or else no federal funds for construction grants is under attack. Elmer B. Staats, comptroller general of the General Accounting Office, has said that the matter of secondary treatment is a matter for Congress to consider in its current attention to clean water amendments. Early this month, EPA will come to some internal position on its turn-key proposal and later in the month will make an announcement.

## **SEC: companies must report environmental effect**

The Securities and Exchange Commission (SEC) will change some of its reporting forms to reflect the requirement that environmental matters are disclosed to investors in cases where they are economically relevant. Final announcement on SEC forms is due this month; it is expected that forms will be filed by 10,000 companies. Recently, SEC Chairman William J. Casey told the House subcommittee overseeing NEPA administration (ES&T, March 1972, p 211) that the change would require appropriate disclosure that compliance with various federal, state, and local laws and regulations will have on capital expenditure, earnings, and competitive position of publicly owned companies and their subsidiaries, including pending and threatened legal proceedings.



SEC Chairman Casey

## **Congress: environmental compacts and noise**

The Senate Public Works Committee has approved the interstate environment compact (S.907). The legislation would permit states involved • to establish regional waste management organization with the necessary authority including capability to incur debt and sell bonds • to implement existing and future water pollution requirement without the lengthy delay often associated with usual compact approval and • to establish air and water monitoring facilities and purchase equipment. On the other side, the House has completed its work on the Noise Pollution Control Act (H.R.11021) which would give EPA authority to set noise standards for transportation equipment, in-plant machinery, and household appliances.

## **Court finds Corps 102 statement adequate**

In a decision of February 14, Chief Judge Eugene Gordon of the U.S. District Court for the middle district of North Carolina, said that the Corps of Engineers, 3-volume statement on its New Hope Dam project in NC fully disclosed all possible environmental effects and fully discussed alternatives. He also said that the court cannot substitute its opinion as to whether the project should be undertaken or not. (For more on NEPA, see ES&T, March 1972, p 209.)

## **State gears up for forthcoming UN conference**

The Secretary of State's advisory committee on the 1972 Conference on the Human Environment last month completed a series of regional meetings on the six topics of the conference. Sen. Howard Baker, Jr. (R.-TN), chairman of the committee, scheduled the regional hearings to gather views and information to help develop the U.S. role.



# environmental currents

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## **STATES VA, DE tackle air pollution; NJ regulates noise**

Virginia Transit Co. will convert all 230 commuter diesel buses in Richmond and 190 in Norfolk to a new fuel injection system. This switch is expected to cut hydrocarbon emissions by 50%, smoke density by 30%, and odor by 40%. New Jersey's Noise Control Act, effective in January, empowers the NJ Dept. of Environmental Protection (DEP) to control noise pollution as it does air, water, and land. DEP can set limits, operation curfews, and fines. A 13-member council, created by the bill, will have veto power over DEP noise decisions. The federal EPA issued a 30-day notice to Delmarva Power and Light Co. (Delaware City, DE) in the first formal enforcement action taken by EPA under the Clean Air Act of 1970. The utility violates Delaware's implementation plan for national air quality standards.

## **Radiation emergencies handled by Illinois team**

The Illinois Radiological Response team, created a year ago by seven IL state agencies, responded to more than a dozen incidents ranging from a lost radium needle at an Illinois hospital to a blown diaphragm on the main release stack at a nuclear power plant. The departments of Public Health, Law Enforcement, Transportation, Agriculture, Illinois Civil Defense Agency, Environmental Protection Agency, and the State Fire Marshall's office formed the response team to control any peacetime radiological incident and to minimize radiation exposure.

## **KY law taps mine water; discharges contested in MN; Field Year**

Kentucky mining companies had until the first of last month to comply with the state's regulation-setting limits on sediment and acidity in water runoff from surface mines. Turbidity is limited to 150 Jackson units (to measure opaqueness). The U.S. Justice Department filed suit against Reserve Mining Co. (Silver Bay, MN) for discharging taconite tailings into Lake Superior. The same case is also in the Minnesota Supreme Court and has been the subject of state and federal actions since 1967. The federal complaint contends that Reserve does not have a federal discharge permit; however, Reserve states that a permit was issued in 1948. The International Field Year for the Great Lakes was kicked off this month. Universities and agencies in the U.S. and Canada began a concentrated study of Lake Ontario.

## **Solid waste buried in Iowa, banned in Oberlin, OH**

A new Iowa regional solid waste disposal agency has closed eight burning dumps and improved collection services in the Des Moines region. Prior to the agency's formation, metropolitan Des Moines collected food waste only, piled it in open dumps inside and outside the city limits, and burned it. Solid waste is now collected and buried in a sanitary landfill. Two of the Des Moines dumps will be converted into parks. The town of Oberlin, OH, enacted one of the most extreme antipackaging laws in the country. Effective in January, the ordinance not only bans the sale of no-deposit beverage containers, but also provides a fine for anyone found possessing such a container within the town limits. The American Civil Liberties Union, calling parts of the ordinance "clearly unconstitutional" plans challenge.



Acid mine drainage

# environmental currents

## TECHNOLOGY Process cuts pollution from aluminum recycling

770,000,000 aluminum cans  
... build 218,747 jumbo jets  
... cover 35,000 homes with siding  
... turn out 35 million lawn chairs  
... make 46.5 million tennis rackets  
or 18 million baseball bats  
... build 130,000 mobil homes

Reynolds Metals Co. (Richmond, VA) has developed a new process for fluxing and degassing molten aluminum that cuts down on chlorine and particulate matter emissions. Fluxing, used when remelting aluminum for casting processes, is a means of purifying molten metal by bubbling gas through it. Generally, pure chlorine gas is used, but Reynolds Mixed-Gas Fluxing process uses a mixture of 10% CO, 10% chlorine, and 80% nitrogen. The efficiency of the method is comparable to that of the straight chlorine method, according to Reynolds, but it is less expensive and cuts pollution at the source. Nearly  $\frac{3}{4}$  of a billion aluminum cans valued at about \$3.5 million were redeemed by aluminum producers in 1971—four times the number redeemed in 1970.

## SO<sub>2</sub> scrubbing process tested

Atomics International (AI—Canoga Park, CA) is testing a flue-gas scrubbing process designed to remove sulfur oxides and particulate matter from stack gases of coal or oil-fired electric power plants. Being tested at the Mohave Generating Station in Clark County, NV, the AI process uses a spray mist of carbonate salts in water to remove sulfur oxides from flue gases. Hot flue gas then evaporates the water, leaving a dry powder which can be melted and, after particulate matter removal, regenerated with carbon and carbon dioxide. The sulfur comes out as H<sub>2</sub>S which can then be converted to salable sulfur. Since the process operates at low temperatures, it could be adapted to most existing fossil-fuel power plants.

## New fiber source interests papermakers

The pulp and paper industry has a promising new raw material in kenaf, a highly productive annual plant which looks a bit like scrub sumac. The plant can be harvested about four months after planting and responds favorably to soda, sulfate, and neutral sulfite-pulping processes. The plant has been grown in Florida and Illinois.



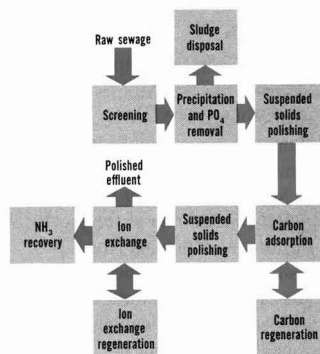
Kenaf

## Breaking up bugs hastens oil spill cleanup

Scientists at Houston Research, Inc., say that oil slick degradation by microbes can be speeded up by mixing fragmented microorganisms with whole ones (See ES&T, May 1971, p 389). The reason: intracellular enzymes get the oxidation of oil off to a faster start, producing organic acids and aldehydes which become food for the intact bacteria. Reproduction rates are thereby enhanced and the job gets done more quickly.

## Physical/chemical plant due by end of 1972

The country's first complete physical/chemical sewage treatment plant has been sold by Graver Water Conditioning Co. to the Metropolitan Sewer Board of the Twin Cities area for the village of Rosemount, MN. The process uses a variety of chemical and physical separation methods rather than bacteria to remove BOD, nutrients, and solids. Sewage entering the plant first passes through trash screens, then to sludge reactor where precipitation of solids and phosphate removal is accomplished. The effluent is polished to remove remaining solids, passed through a carbon adsorption unit to remove organics, filtered again, and subjected to ion exchange to remove ammonia.





## **INDUSTRY** Industry's bill for pollution control is tabulated

Results are now in on the microeconomic studies announced earlier by CEQ, EPA, and the Department of Commerce. The total investment facing 25 major manufacturing industries in the U.S. is an expenditure of \$32 billion between 1972-76. In the air category, the cost estimate assumes compliance with the national air quality standards and in the water category the industrial equivalent of secondary treatment. In addition, the public sector and federal, state, and local governments are faced with an expenditure of \$70 billion. At a CEQ briefing, it was noted that no industry including the big four—steel, paper, petroleum, and electric utilities—will be severely impacted. Of 12,000 plants studied, some 800 are expected to close in the 1972-76 period due to marginal profit operations and for rising cost per unit production; another 200-300 are expected to close because of pollution control requirements. Last year, 13 plants closed; 38 are expected to close in 1972 but the reasons for closing, whether economics or pollution control requirements, simply are unknown.

### **Ethyl Corp. executive opposes lead controls**

"The findings of the recent National Research Council document entitled 'Airborne Lead in Perspective' do not support the EPA's proposed requirement for a 60-65% reduction in lead emission from motor vehicles," says F. D. Gottwald, Jr., chairman of the board of Ethyl Corp. According to Ethyl Corp., the EPA-proposed regulations are without scientific or technical justification. Gottwald adds, "The proposed regulations assume the availability of a catalytic converter despite the fact the major automobile manufacturers all have stated at recent congressional hearings that they do not have catalytic devices capable of meeting the 1975-76 federal exhaust emission standards."

### **Northwest pulp and paper industry sets cleanup pace**

Mills in Washington and Oregon are leading the pulp and paper industry in their cleanup progress. Seventy percent of their capital expenditure goes for air and water pollution controls whereas nationwide, The investment in capital equipment for the entire pulp and paper industry is 33%. Donald Benson, executive secretary of the Northwest Pulp and Paper Assoc., says that the mills in these two states are well past the halfway mark in antipollution capital investment program that will total nearly \$350 million by 1975. Benson also noted that the national costs to meet a zero discharge standard would amount to an annual per capita cost that would exceed those of police protection, education, and public welfare.

### **Industries need to be innovative**

Industries faced with seemingly impossible pollution control dilemmas may find relief in recently issued patents which cover a wide array of subjects: • jet engine • noise suppressors • nonpolluting electric power plants • stack afterburners • sewage treatment methods • recovery of waste paper treated with urea • antimog carburetors. Commissioner of Patents Robert Gottschalk says that in the patent office's two years of priority processing of antipollution inventions, 666 applications were granted the accelerated processing status and that 230 have been approved for issuance.



Donald Benson



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# Stewart Udall

*A stimulating chat with the founder of the Overview Corp. and one of the originators of the bold new concept of total environmental planning*

*Stewart Udall is chairman of the board of Overview Corp., an international environmental consulting firm with offices in Washington, DC, San Francisco, and Honolulu. Former Secretary of the Interior in the Kennedy administration, noted conservationist, lawyer, author of "The Quiet Crisis" (1963) and "1976: Agenda for Tomorrow" (1968), Udall tells ES&T's Stan Miller that the bold new approach—total environmental planning—is redefining business progress in the broadest terms, not only in the U.S. but in a worldwide context, and that Overview is perhaps five years ahead of its time.*

## **Organization**

**What are the highlights and achievements of Overview since it was formed in early 1969?**

Overview is one of the more fulfilling things that I am doing, but it's not the only thing. About half of my time is Overview and the other half is lecturing and writing a syndicated column with an associate.

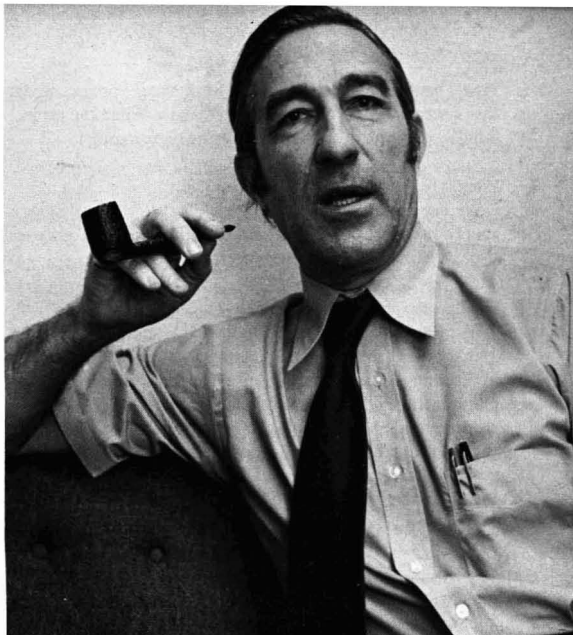
Three years ago, Overview started with a lot of ambitious ideas. I wasn't quite sure then that this country and others were quite ready for us. Because Overview has not gone into the international field in the way that we had hoped, there is still a lag. In that sense, Overview has gone at a different pace and in a different direction, but we have had considerable success in doing what we believe in—what we call total environmental planning. I think Overview has had some of the most interesting planning jobs in the U.S. We are doing a type of planning in which very few other organizations are interested. We are almost in a class by ourselves. We always insist that Overview will only study something in a total environmental context.

**What do you mean by total environmental planning?**

This concept means that we won't look at any problem in a narrow sense because we think that this is what has gotten this country into much trouble—that is the specialist, single-minded approach to major development projects, be it a highway, airport, or electric power generation.

**What can you tell us about some planning that Overview has studied?**

Our major jobs have included looking at the superjet port that was planned near the Everglades. Overview advised Dade County, FL, on that project which was done in our first year,



1969. We have done a one-of-its-kind study for one of the largest electric power companies in the U.S.—Southern California Edison. In the electric power study, which was finished a year ago (1970), Overview looked at the problems that the utility would face in 1980, 1990, and so on. The study was not a look at the current controversies and problems facing the company. Electric power companies operate on a seven- or eight-year lead time. They have already made a lot of decisions on current problems.

The utility company has chosen to treat the Overview report for their eyes only, but it is the kind of study more and more companies should be doing. Overview, in its studies, is trying to point out new alternatives, solutions that avoid environmental crunches with conservation organizations. It's a kind of preventive planning. We have done other work in the electric power field, a field in which we are interested in particular.

Last year (1971), we concentrated much of our effort on a comprehensive land use and open space study for the state of Hawaii. This year we are just beginning a new study in the field of open space and parks in the San Francisco Bay area for several of the local governments. Of course, the two most interesting places in the U.S. to plan are the San Francisco Bay area and Hawaii because there has been more advanced thinking; people are readier for advanced planning there than most other places.

**With how many international environmental consulting firms does Overview compete?**

Overview is a planning organization. We are different from many other organizations. In a literal sense, I don't think we have any competition. We're kind of unique. We have a small headquarters group, essentially five people. When we got our job in Hawaii, for example, we put together a special planning team in Honolulu designed for that particular job. They were mostly young people. Our project director was Harry Garnham, a young (30 years old) landscape architect. The other people were young residents of Hawaii. We are doing the same type of thing in our San Francisco Bay study.

As I mentioned before, Overview is different from other organizations. Most architects and planning firms have a large staff; they do all the work in-house. One of the Over-

view's new approaches is that we form special project teams that are particularly qualified to do the job. When the project is finished, the team disbands, and we go on to another.

**What is the tax status of the Overview Corp.?**

We are a profit-making corporation. We plan to have a nonprofit foundation so we can do other kinds of projects also, perhaps as we get a little bigger.

**What are the main objectives for 1972?**

We are working on four studies right now, including a second project in Hawaii and another project with an electric power company that will fall in place soon. But we are not interested in building ourselves into great size; we're interested in doing total environmental planning for the type of clients who are willing to accept us on our own terms.

**Advice**

**What advice has Overview given to its various clients?**

Our clients have essentially been government and industry. We just finished a study late last year (1971) for a large petroleum distributor on Long Island, NY. Overview gets into a wide variety of things. They range from site location and transportation and energy corridor studies to the open space and other land use studies. We help our clients act boldly both by examining the broad alternatives that are open to them and then developing a comprehensive action plan (our recommendations) that can make the report a reality.

Most of our clients have come to us on their own initiatives. We have turned down a lot of proposals, particularly when the client wanted to get us in the middle of some sticky fight they already were involved in. We are choosy about what we do and we want to do it our own way.

In Hawaii, Governor John Burns invited Overview to do the study because the state wanted to do something special. We think that much of the planning in the past has been simply planning by planners for planners. Overview, on the other hand, is action-oriented. With our plans, we try always to do the follow-through, to give the plan a fighting chance to succeed. In my opinion, we prepare the kind of report you would rarely see. The Hawaiian report was written for the eyes of the legislators and I presented it to the Hawaii legislature personally this January. A specific legislative program is recommended in the report.

**What advice did you give the Suffolk County state legislature on the oil tank farm?**

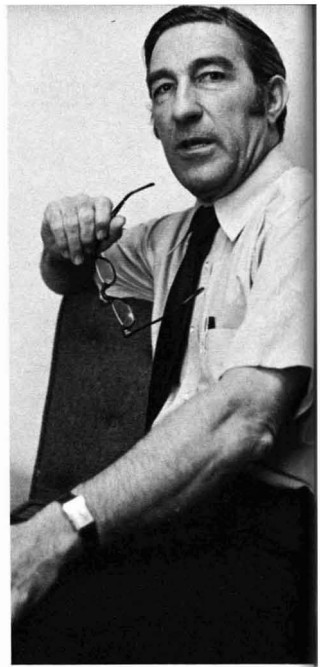
When the petroleum company came to us with their problem—how to site a tank farm on Long Island and build it with the best environmental safeguards available, we began by looking at the general purposal in the context of their region. The pipeline distributors are part of a region, part of a community, part of an environment. Then we zoomed in on the specific problem, developed a set of environmental design criteria, site location criteria, and performed an environmental mapping inventory of the region, vis-a-vis petroleum distribution for the future. I personally presented the report publicly to the Suffolk County Commission on Marine Resources.

**Does Overview provide testimony before congressional committees?**

Overview is not in the field of providing testimony before congressional committees. I do testify quite a bit myself as a private citizen and as a member of national environmental

*"We're interested in doing total environmental planning for the type of clients who are willing to accept us on our own terms."*

*Overview's Udall*



**OVERVIEW**

and conservation organizations. I am on the board of a half-dozen leading organizations including the Environmental Defense Fund and the National Wildlife Federation. I served on the board of Peabody-Galion for two years, that was not an Overview function; I came off their Board in 1972. They reorganized and now have a forward-thinking group of young executives. As a citizen, for example, I testified on the Trans-Alaskan Pipeline on behalf of conservation organizations, not Overview.

**Has Overview provided advice to other U.S. governmental agencies, to foreign countries, to developing countries?**

No, we have made some proposals, but we haven't got in this field yet. Developing countries are more interested in getting industrial development started. They are not at the stage yet where they feel they must face up to pollution control and long-range environmental planning. I am convinced that it is coming in the next few years, but the developing countries are not at that point today.

**Can you describe some new institutional concepts that are making headway in the environmental arena?**

Total environmental planning is perhaps the nearest and newest concept that was pioneered by Overview. It is a concept that we are still defining in practice; here and again you will find it expressed in our reports. We don't think that any planning is really relevant or useful unless it is done in a total environmental context—unless you look at the problem of the clients in regard to how they and their activities fit into the region, the environmental constraints of the region, and so on. Our intention is to put our clients into a position where they understand the practical meaning of ecology and environment and where they can look the people in their community or their region in the eye and say we had solid studies made, we are trying to fit ourselves into the environmental future of the region and we are trying to do the very best we can to help preserve the values that really count. We think enlightened companies are trying to do such planning today, to adapt and change and make efforts to move with the environmental movement rather than fight it.

## Real challenges

### What is the distribution of funds for environmental problems facing industry?

It's obvious that in order to come in with progressive solutions, industries must stop thinking they can cut corners and always do things cheaply. The kind of superior solutions that environmentalists are demanding all over the country is going to cost more money, and all of industry is finding that pollution control and building safety factors into nuclear plants, just to mention two, are going to cost more money to do them right. Essentially, the environmental issue is raising national expectations, and combined with that, raising the standards of performance in industry. In some industries, environmental reforms may be possible with an additional 2% in capital investments. With others it may take 10%. This varies from industry to industry. The important point is that the new laws—and the public is demanding that the U.S. shift gears—move to a new kind of technology, a clean technology, that minimizes the harm to the environment.

### Electric utilities and automobile manufacturers are two industries faced with strict pollution control requirements. What foresight does Overview offer for the solution of pollution controls facing these industries?

I have confidence that major industries in this country can meet the deadlines that are set for them. In general, these industries have the resources, but they have to be pushed. Detroit will not move quickly unless we as a nation push them. Overview had some brief conversations with Bill Lear, who's been working on this steam engine. I think it's very promising. I think his development is certainly a mark against Detroit; they're now turning to the Wankel engine which was invented by a German. To think that the best work that has been done in this country on a new engine has been done by Lear spending his own money! What happened to the Henry Ford spirit in Detroit?

The public is insisting that the U.S. have the cleanest and best electric power system that is possible, the cleanest most environmentally satisfactory automobile that we can manufacture. I don't think enlightened industry people are fighting this now; enlightened industries are moving ahead. People like myself are going to continue to push for the kinds of solutions that we know engineering and technology can provide. Industries have got to be innovative and be willing to move rather rapidly in some instances. In my opinion, it is going to be a damn shame if industry blocks someone as creative as Lear, and the government doesn't give him the (financial) encouragement that's needed to see whether he has one of the answers to the automobile manufacturer's dilemma.

## Federal initiative

### Are you satisfied with the track record of the Environmental Protection Agency?

I thought that EPA as a watchdog agency was a good idea at the time it was formed. I still think that EPA is right organizationally, but EPA has a rather mixed record. I don't think it fully met the nature of the crisis. It has done some good things but has tended to be wrong on the big ones, like the SST, for example. The Nixon administration plans to go ahead with the Alaska pipeline, but I think it will regret it before we're through. The Nixon administration has provided some new leadership; it certainly deserves credit for that.

### Can you say the same for the Council on Environmental Quality?

CEQ is filling an important role. I believe CEQ has been a good development. Essentially, my former department (Interior) was doing this three years ago. Now, the President has advisers who are working on it every day. I do wish CEQ would be able to get the President's ear on more issues. I also wish that CEQ was a bit more aggressive.

One of the best things CEQ did last year was urging the President, and he listened to their advice, to stop the cross-Florida barge canal. There are a lot of other projects that are just as bad that CEQ could stop if it were more aggressive.

### Are you satisfied with the cleanup progress that is being made under existing federal environmental laws? Are you satisfied with the cleanup progress, for example, in water?

No, the U.S. is still floundering. We floundered back in the 60's when I look back at it. Still, the U.S. is not moving fast enough. Overall, our air and water are dirtier today than a year ago. Until we can say and document that we are actually cleaning up the country, the public has to be concerned about it. There must be tougher enforcement and probably more federal help such as incentives for industries. Some of these industries are moving at a good clip on cleanup programs, but the majority are still dragging their feet, trying to postpone the investments they must make.

### How important will the environmental issue be this election year?

Environment is in the big time now. It is no longer a peripheral issue. The environmental issue touches so many aspects of American life that I think in one way or another, it will be one of the top five, certainly the top 10 issues, discussed. The performance of the Nixon administration will be part of the debate along with the environmental promises that both parties make.

### What are your comments on NEPA?

The National Environmental Policy Act is the most significant law of the last three years. It is one of the most important laws passed this century when it comes to conservation and the environment. NEPA has certainly done more to make us shift gears and take the environmental revolution seriously than anything else that has happened. NEPA has had a broad impact in making us try to redefine progress in this country. That is what we're in the process of doing, whether we think of it that way or not.

## UN Conference

### Did Overview participate in any planning for the forthcoming UN Conference on the Human Environment?

No, as you know, the organization has been largely governmental. I participated personally in a sort of preview conference (last summer) with the government of Finland.

### In your opinion, what are the top items that need to be addressed at this conference?

The main danger is that the conference will end up just as a talk fest, and talk is cheap these days. The main issue is whether the United Nations is going to organize itself and set up new institutional arrangements to deal with the environmental crisis. For example, the UN should exercise jurisdiction over the oceans; it should manage the oceans, protect them, levy taxes on the commercial traffic that moves across them. In this sense, I am for a bold plan of action.

# Tube settlers up clarifier throughput

*Ranks of inclined plastic tubes could save the day for overloaded water treatment plants if they perform as well in long-term trials as they have in pilot studies*

Here's the answer to a waste treatment plant operator's dream—how to double the capacity of his clarifier at a mere fraction of the cost of installing a second one.

New technology? Actually, it's more like refined technology. The prototype unit was built around the turn of the century. There was only one problem—it didn't work very well.

The flat, parallel plate settler, first built in 1904 has given way to the inclined tube settler—which works very well indeed. It works so well, in fact,

that in pilot plant operations, and the initial industrial field installations, it has been possible to double flow rates through a clarifier without impairing effluent quality. And in most clarifiers, it's possible to install an inclined tube settling module in existing equipment without adding to space requirements.

### How it works

To understand how the inclined tube settler works, imagine a cylindrical tube, 1-in. in diameter and 10 in. long, filled

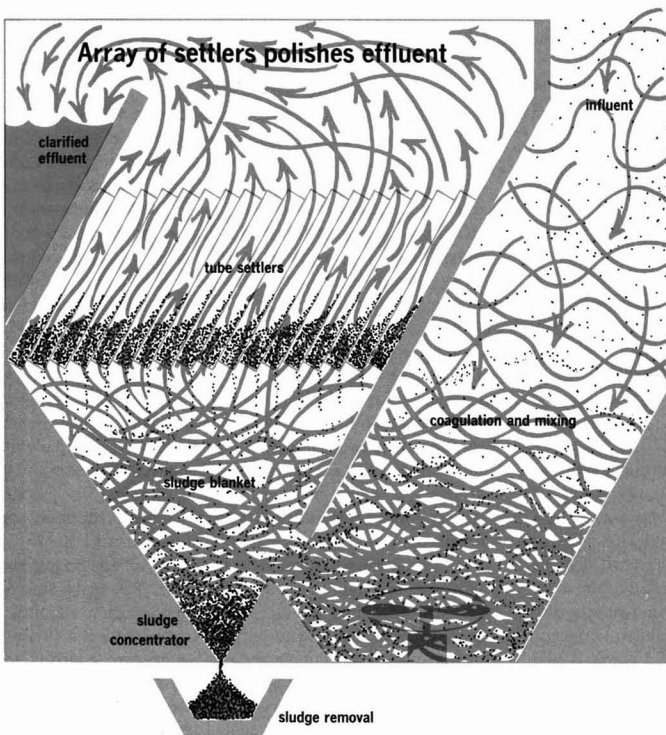
with liquid in which settleable solids are suspended. If the tube were shaken and then held vertically, solids would have to travel almost 10 in. before coming to rest on the bottom. If, on the other hand the tube were held horizontally, the solids would have to travel only 1 in. to settle out. Settling in the horizontal tube would be approximately 10 times faster than in the vertical tube.

The problem with the horizontal tube—and with the earlier parallel plate settler as well—is that the tube quickly becomes plugged with solids. To avoid that, one could tip the tube—incline it—and the solids would slide out the bottom.

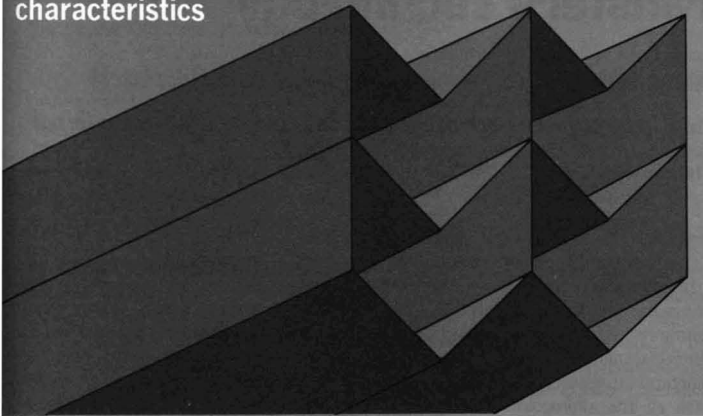
To make a continuous system, one would need only to cement several tubes together, incline the entire bank, and introduce at the bottom particle-laden water which would flow upward through the tubes. Solids would settle out, slide down the tubes and out at the bottom, and clarified effluent would be discharged over the top. Add a few minor engineering niceties and the result is a module which upgrades the efficiency of a precipitator system considerably.

A fairly typical configuration of the tube settler unit installed in a precipitator is shown at left. Waste water is introduced into the coagulation chamber along with suitable conditioners and flocculating agents and mixed by a rotor on the bottom of the tank. As coagulation proceeds, a sludge blanket is formed below the tube settler module. Flocculation is completed in the sludge blanket. Smaller particles become attached to larger particles rather than being carried out with the effluent. Sludge solids tend to collect in the bottom of the unit where they may be concentrated and removed.

As the effluent rises through the tube settler module, settling occurs in about the first one third to one half of the tube length, solids drop back into the clarifier, and clarified effluent spills out



## Chevron configuration of tubes gives optimum settling characteristics



the top of the tubes and into the discharge stream.

### Tube design important

Although the settler concept is basically a simple one, performance depends heavily upon tube design. Flow characteristics are important because, for settling to occur, liquid flow needs to be laminar, and turbulence must be minimized. In the bottom section of the tube, flow is largely turbulent. As drag exerted on the liquid by the walls of the settling tube increases with tube length, turbulent flow changes to laminar flow.

Flow rates through the tube can be increased as long as the laminar flow characteristics are not upset. Generally, the higher the flow rate, the smaller the tube diameter (and therefore the higher the surface area on the liquid in proportion to its velocity) must be.

The flow characteristics of a tube are optimized by relating them to the Reynolds number, a dimensionless number which describes the general flow characteristics of a liquid through a tube. (With a Reynolds number less than 2100, flow is usually, but not necessarily, laminar. With a Reynolds number greater than 2100, flow is necessarily turbulent.)

The Reynolds number is related to fluid characteristics by the equation:

$$Re = \frac{D\rho V}{\mu}$$

where  $D$  is tube diameter,  $V$  is velocity of the fluid,  $\rho$  is the density of the fluid, and  $\mu$  is the viscosity of the fluid. The above equation holds true for circular tubes. For noncircular tubes, the equivalent

diameter is substituted for the tube diameter, according to the equation:

$$\text{Equiv diam} = \frac{4 \times \text{area}}{\text{perimeter}}$$

Since the highest velocities are obtained by decreasing the equivalent diameter, the optimum shape of the tube is one with a cross-sectional area of maximum perimeter.

Tube shape is also an important consideration in determining settling characteristics. The tube height should be as short as possible to minimize settling distance. Uniform settling distance is desirable so most particles have the same settling time. Circular tubes, for example, are not efficient because particles entering at the top of the tube have a greater distance to settle than those entering at the sides.

Tube shape should permit nesting so that there is no wasted space between tubes in the unit. Again, circular tubes are not particularly efficient because of the large amount of dead space between tubes in the settler array.

One design which maximizes settling characteristics is the Chevron design, according to William A. Beach, research associate for The Permutit Co. Permutit's Chevron Tube Settler module is an array of nested 24-in.-long extruded polystyrene tubes with a cross-sectional chevron shape (see diagram). The 1-in. chevron configuration, Beach says, has the highest perimeter of any common shape of the same area. Tube height is less than tube width and settling distance for particles entering anywhere along the top of the tube is the same. An added advantage, according to

John R. Anderson, Permutit's vice president for research and development, is that the v-groove promotes optimum sludge compaction and flow.

From studies in pilot installations, and about a dozen industrial field installations, Permutit is optimistic that the tube settlers will provide significant improvement over existing conventional clarifiers. With proper engineering and design, Beach says, clarifiers can operate at rates between 4 and 5 gpm/ft<sup>2</sup>. Without tube settlers, these same clarifiers are only rated at about 1-1.5 gpm/ft<sup>2</sup>.

### Markets

Despite their promising future, one wonders why tube settlers are not more widely used today. Besides Permutit, at least two other U.S. companies (Graver Water Conditioning Co. and Neptune Microfloc) market proprietary tube settler units. Several installations are successfully operating in Canada, according to William Wachsmuth, president of Ecodyne, Ltd.

The main reason for the relatively poor market penetration, Beach says, is that the technology has been refined only in the past three years. Although there are a handful of operations scattered around the country using tube settlers, Permutit prefers to await further field testing before launching a major marketing effort. Still unanswered, Beach says, are questions of longevity. How, for example, will the buildup of algae or precipitates on walls affect the units' performances?

Furthermore, the units have not been tested on a wide variety of industrial process effluents—although there is no reason to expect that they would not do well, judging from preliminary data. Applications in municipal areas are similarly not well tested, although it appears that tube settlers would best be adapted to polishing secondary effluent rather than primary effluent. HMM

# EPA program transfers technology

*Establishing a two-way street between municipal users and federal producers of new technology whereby municipal needs are satisfied by the federal RD&D products*

EPA's technology transfer (TT) program is primarily aimed at marketing the products of the federal research, development, and demonstration (RD&D) activities, (ES&T, June 1971, p 498). The products include design seminars, design manuals, and an array of communication items including videotapes, visual displays, and publications.

The TT program has come a long way since it was first announced by David Dominick (then Commissioner of the Water Quality Office and now EPA's assistant administrator for Categorical Programs) at the Boston meeting of the Water Pollution Control Federation in the fall of 1970. Future plans for the program include expansion into other major environmental areas including air, industrial waste water, and solid waste. The expansion of the TT program is in line with current plans to include research, development, and demonstration of both air and solid waste under the aegis of the assistant administrator for research and monitoring, Stanley Greenfield. These plans will be accomplished after this July 1.

The initial goal of the TT program was to make an impact on the construction of municipal waste treatment facilities over the next 3-4 years. The need for the program was first recognized by Eugene Jensen (now head of EPA's water programs office) and David Stephan (now on Greenfield's staff) in the middle of 1970 and before the Boston announcement. At that time, these officials recognized that applications for construction grants were not including new technologies, thus the need for a special TT effort. Within the new organization of EPA, Greenfield appreciated the significance of the program and elevated it to function from his immediate office, in order to allow for its expansion into other environmental problem areas.

## Products

To date, design seminars have focused on the waste water treatment problems in EPA regional areas (see map). For example, phosphorus removal may be a prime target in one region while

upgrading existing sewage treatment plants might be the top target in another.

In any event, each of these seminars brings together approximately 100 consulting engineers, sanitary engineers, and municipal engineers. The objective of the program is to ensure that these engineers have all the alternatives and options open to them in designing today's waste water treatment plants.

By the end of last month, a dozen such design seminars had been held in each of the 10 federal regions with the



**EPA's Robert Crowe**

*... marketing federal RD&D products*

exception of region VIII (Denver); however, the first seminar for fiscal 1973 is slated for Denver, and the near-term schedule for the remainder of this fiscal year includes seminars in Washington, DC (this month); up-state NY (May); and Pittsburgh, PA (June).

"During the remainder of this calendar year, it is anticipated that at least one design seminar will be held every month at the requests of the regions," says Robert Crowe, special assistant for the TT program, who reports to Greenfield, the assistant administrator for research and monitoring.

"We are not trying to design waste water treatment plants," Crowe says. "We are not in the consulting business, or in the design business, but we want to make sure that both the consulting and design engineers, along with the administrative decision-makers and the

public have all the alternatives and options of new technology available to them," he explains.

"The TT staff has worked closely with the Consulting Engineers Council (CEC) and the Water Pollution Control Federation (WPCF) and continues to seek their guidance and advice in order to maintain relevancy of the TT program," Crowe says.

Process design manuals are the backup material at the seminars; the manuals are loose-leaf volumes and represent all of the available, usable, and practical technology to date. These manuals are prepared by consulting engineers most knowledgeable in the field and the research staff of the Office of Research and Monitoring. They will be updated as the needs arise.

Four manuals have so far been prepared and distributed; they cover the subjects of physical-chemical treatment, upgrading of existing sewage plants, phosphorus removal, and carbon adsorption. At press time, some 20,000 copies of the manuals had been distributed (5000 of each manual) and an additional 6000 individual requests for the complete set of four have been received.

The design manuals are not a duplication of the efforts of the Water Pollution Control Federation (WPCF) but a necessary adjunct to WPCF publications. "We are not in competition with WPCF's manuals; ours are written as a supplemental text to theirs," Crowe says.

Three other design manuals are planned, one on sulfide control in sewage systems, which will get at the odor and corrosion problems in waste water treatment plants, a second one on sludge handling and disposal, and the third on advanced techniques in operation and maintenance.

A videotape on carbon adsorption is another tangible product of the TT program; each EPA regional office has a copy. A second videotape on phosphorus removal is being prepared.

To design a meaningful program to transfer technology to administrative decision-makers, the headquarters team



of the TT program is working with a group called Public Technology, Inc. "PTI hopes to function as a focal point for response to the city's need, and we are working with them now to get inputs from the cities and meet with their managers," Crowe says. "We are working primarily with Robert Havlick, a senior vice-president of PTI." PTI is sponsored by a half dozen of the major public groups including the Council of State Governments, the National Association of Counties, the National Governors Conference, the National League of Cities, the U.S. Conference of Mayors, and the International City Managers Association.

"We can see that our (EPA) relationship with the cities will be a two-way street where, in one direction, we will transfer technology to them and, in the other direction, we will know their

needs so that EPA research can work toward solving their problems."

#### Staff

In addition to the staff of a half dozen professionals at the headquarters office, there are staff members at the National Environmental Research Center (NERC) in Cincinnati and the regional chairmen for the TT program; they contribute significantly to the program.

In addition to Crowe, members of the headquarters TT team include Robert Mandancy, who is responsible for evaluating new technology for introduction into the program, John Dyer who is responsible for the seminars and is concerned mainly with the technical presentations, Denis Lussier (technical publications), Paul Minor (industrial waste treatment), Kenneth Hay (communications resources), and Bill Herbert

(administrative assistant).

Depending on the specific problem being addressed at any one particular design seminar, a member of the NERC team introduces the subject to the attendees, presents the EPA experiences, and is on hand to answer questions as they develop, since these EPA personnel are the most knowledgeable in the agency on the specific subjects presented. The Cincinnati team members and their specialties include, for example, Ed Barth (nitrogen and phosphorus removal); John Smith (upgrading sewage treatment plants); Carl Brunner (carbon adsorption and phosphorus removal); Sid Hannah (solids removal); Jesse Cohen (physical-chemical treatment); Irwin Kugelman (physical-chemical treatment and phosphorus removal); Art Masse (carbon adsorption); and John English (carbon adsorption). SSM

**Contact for 10 federal regions**

Region	Technology transfer chairman	Region	Technology transfer chairman
I	Lester Sutton (617) 223-7210	VI	George Putnicki (214) 749-3842
II	Rocco Ricci (201) 548-3441	VII	Lynn Harrington (816) 374-2725
III	Warren L. Carter (215) 597-9410	VIII	Stan Smith (303) 837-3769
IV	Asa B. Foster, Jr. (404) 526-5784	IX	Irving Terzich (415) 556-7554
V	Clarence Laskowski (312) 353-1056	X	John E. Osborn (206) 442-1266

*An innovative educational program in water pollution control at the headquarters of a large aerospace company is ambitiously aiming to provide . . .*

## New skills for out-of-work engineers

Can unemployed aerospace engineers find happiness—and, more important, a job—in pollution control? That question has grown in importance as the extent of unemployment among engineers in the U.S. has become more apparent. Unfortunately, especially from the point of view of engineers pounding the pavements from San Diego to Boston, the answer is far from clear.

Perhaps, the fate of 21 engineers who have just completed a six-month retraining program in water pollution control at the Bethpage, NY, headquarters of Grumman Aerospace Corp., will help clear up the presently fuzzy picture.

Unemployment in the aerospace industry is not entirely a recent phenomenon, of course. Employment rolls have been dwindling for several years, ever since completion of the major projects which resulted in, among other things, the landing of men on the moon. The seriousness of the unemployment problem was officially recognized by President Nixon in April 1971. At San Clemente, CA, the President instructed the Department of Labor to set aside \$42 million for a program to assist unemployed aerospace professionals in 11 hard-hit areas of the country to retrain and relocate in other industries.

Twenty-five of this \$42 million was earmarked for on-the-job or institutional training or retraining. The program itself now bears the title, "Technology Mobilization and Reemployment Program for Engineers, Scientists and Technicians" (TMRPEST).

Development of a retraining program at Grumman was spearheaded by Arthur Gilmore, himself trained as an aeronautical engineer, and now Grumman's director of training and development. In 1970, when it became clear that a hoped-for turnaround in the aerospace industry would not materialize, Gilmore began to think in terms of a short-term conversion program in which aerospace engineers might be retrained for water pollution control-related projects. (Grumman had already developed some capability in the field, exemplified by the waste water recycling system built into the Apollo Lunar Excursion Module.)

Gilmore originally contacted the Environmental Protection Agency in Washington with a view to getting federal assistance for a retraining program, but this assistance was subsequently refused because Grumman was a private, profit-making firm. At the same time, Gilmore was in contact with the civil engineering faculty of Manhattan College, New York, members of which gave advice on curricula that might be useful in a retraining program. He also contacted the New York State Department of Environmental Conservation in Albany to determine how many, if any, suitably retrained engineers the department might be able to employ in 1971. The answer from Albany was not optimistic, largely because budget money was expected to be hard to come by.

In late 1970, Gilmore sent a questionnaire to a large number of potential employers of water pollution engineers in the New York City-Long Island area—consulting engineering firms, county health departments, and the federal EPA office in Edison, NJ. By March 1971 he had established that these firms and agencies would probably employ as many as 120 engineers in 1971. Answers

to the questionnaire also established what subjects should be taught in an engineer conversion program.

In March 1971, after learning that federal EPA funds would not be available, Gilmore contacted the New York State Employment Service in Hicksville, Long Island. Through that office he discovered that federal funds might be available after all—from the Labor Department's \$25 million TMRPEST fund. The Hicksville office subsequently assisted Grumman to apply for funds through the state government in Albany, a type of grant-funneling arrangement now common under federal government decentralization policy.

By the time the \$40,000 project was formally approved in August 1971, Gilmore's department was ready to go with a six-month retraining program beginning in September 1971 and running until March 1972. Provision was made to enroll about 20 engineers.

### The retraining program

Students for the program were selectively screened from about 160 resumes on file with the Hicksville office. Assisting Gilmore in making the selection of students were a consulting engineer and a state official. The key factors they were looking for in a potential student were a suitable educational and work background and a real desire to move into the water pollution control field. In order to qualify, each engineer also had to be a resident of New York State, a veteran, and unemployed for at least five-six months. Twenty-three students actually started the course in September, but two later dropped out.

The course in all involved over 600 hours of instruction in subjects ranging from microbiology to instrumentation (see box). Students attended from 4-5½ hours of class daily from Monday to Friday, with the first class generally starting at 4 in the afternoon. The instructors were largely drawn from Grumman's professional staff, but included two local consulting engineers for the design courses.

### A varied curriculum for engineer retraining

Introduction to environmental engineering	52 hr
Chemistry class	52
Chemistry lab	78
Hydrology	117
Microbiology class	52
Microbiology lab	78
Instrumentation and data processing	36
Water supply and water treatment	156
Total	621 hr

Also provided: tours of treatment plants and job seminars.

The students themselves were originally educated in a variety of disciplines, with the majority being either mechanical or electrical engineers. Ironically, only one had received formal education as an aeronautical engineer. Most were in their forties, and nearly all had families to support. Of the 21, 11 had at one time or another worked for Grumman.

Student reaction to the course seems generally to have been good. However, the students were most cautious in assessing their chances for a job in their newly chosen field. "Right now, money seems to be just as tight in the environmental area as anywhere else," Philip Burton, 46, a former chief engineer with Gyrodyne Co. of America, told ES&T in the course of a mid-February visit to the program. Burton would prefer to stay in the Long Island area, but most other students said they would be ready to relocate if a suitable job were offered.

Gene Clark, 44, an electrical engineer with a master's degree in business administration, expressed the typical student's approach to the program: "I have no apprehension about learning new things. Life is a constant process of education."

In fact, their desire to learn seems to have made the students an ideal group to instruct, according to Bill Jamieson, a Grumman staff member who taught the microbiology class. Some, he says, were very good students.

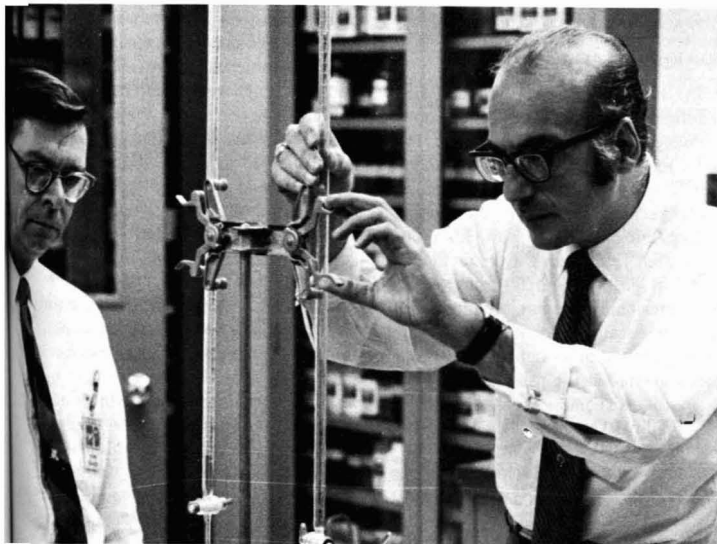
One of the facets of the course that Gilmore considers most important was a once-weekly employment seminar at which students were told of the types of jobs done in different agencies and consulting firms. Although the students felt that the course would equip them very well for filling these sorts of positions, they remained wary about their attractiveness to potential employers: "We have no illusions about short-term pos-

sibilities," said Bob Brennan, at 39 one of the younger members of the class, but all the students felt more optimistic about long-term job hopes.

All, too, were obviously very much aware that it will be an uphill fight to get a job in the water quality field, despite the efforts of their instructors and of Gilmore and his staff. They felt that they have been done much harm by having been lumped together as "aerospace engineers," tagged as prima donnas, as having been consistently overpaid, and as having no appreciation for budgets or time schedules. They particularly resented the implication that it would be beneath their dignity to accept the salaries likely to be offered them in the environmental field. They pointed out that they have a good idea of the salary ranges obtainable from their weekly job seminars during the course. Unavoidably, of course, these will on average be lower than the salaries the students commanded in their previous jobs.

At deadline time for this issue (second week in March), eight of the engineers who finished the Grumman course have been made concrete job offers. How these men fare in the job market will go some way to answering the question whether retraining can equip a man with tools that will truly serve him well in a new field. But it may not dispel a lingering suspicion that the pollution control field is still not in a position to absorb large numbers of engineers however well they have been trained or retrained.

The Grumman program appears to represent just about the best sort of retraining an engineer could hope for, both in quality of instruction and length of program. If graduates from this program are unable to find employment, critics of all retraining programs will undoubtedly intensify their cries for an alternative approach to putting unemployed talent back to work. DHMB



**Students again.** (above) Mechanical engineer Frank DiCuia performs a titration in chemistry laboratory under the watchful eye of instructor Robert Holden. (at right) Afternoon class convenes to listen to City College of New York professor Gerald Palevsky talk on the subject of hydrology engineering



*Deputy assistant administrator Samuel Hale, Jr.  
of the Environmental Protection Agency  
explains to ES&T readers the . . .*

## Federal redirections in solid waste

At first glance, the budget request figure of \$23.3 million for the solid waste management program of the Environmental Protection Agency (EPA) in fiscal year 1973 would indicate a substantial decrease in the funding activity in this critical environmental area. But upon talking with Samuel Hale, Jr., the bright, young deputy assistant administrator for the program, ES&T learned that the office will have more than \$35 million, assuming that the budget request is appropriated by Congress.

Hale explains, "Basically, the solid waste management office still has some unobligated fiscal year 1971 money and a lot of fiscal year 1972 money that has not been obligated. These funds, when added to the fiscal year 1973 request, give the Office of Solid Waste Management Programs a total of \$35 million. In addition, there is another \$5 million for solid waste research under the assistant administrator for research and monitoring, Stanley Greenfield. This total (\$35 million) is about as much money as we are going to be able to spend very well, essentially in about 15 months."

With one exception, the funding level for 1973 was held at a constant level with the 1972 funding level, the exception being, of course, so-called Section 208 funds (after the new section in the Resource Recovery Act of 1970, P.L. 91-512). These funds are for full-scale demonstration of resource recovery systems. In the past two years, two supplemental appropriations were made for these systems, a \$4 million supplemental in 1971 and an \$11 million supplemental in 1972. "None of these funds has as yet been spent," Hale says. "So, this entire \$15 million 'carryover' fund will be available for fiscal year 1973."

"We are undertaking a major redirection of our solid waste management activities," Hale says. "Between now and June 1973, we will be concentrating our energies primarily on taking what we know now and using that knowledge to get improvement now in local solid waste management practices to demon-

strate that many of the solutions already are well in hand and can be readily adopted at the local level without substantial federal financial assistance. To the extent we invest in acquiring new knowledge, except for our resource recovery demonstrations program and a couple of other areas, we intend to invest predominantly in learning more about practical, immediate-payoff, general inexpensive improvements—in sanitary landfill design and operation, in how to get capital financing, in how to reduce collection costs, in solving market obstacles to resource recovery, and so forth."

### Barriers

In Hale's opinion, political, institutional, financial, and other non-technological barriers have been the most important obstacles to the adoption of progressive solid waste management practices. "Obviously, if a town is running an open dump now, it's quite likely that it will have to incur higher costs to dispose of its wastes in an environmentally acceptable manner; this is a practically unavoidable cost increase. On the other hand," says Hale, "most people in the program feel confident that we could go into the average city or town and help them find ways

to save 20% or more in collection costs (which generally account for about 75% of a locality's total solid waste management costs) through such simple means as more efficient routing, more balanced truck crews, and so forth.

The resources of the solid waste management program, then, are being redirected to focus on what Hale sees as the barriers to change. "I've stated that the program will be concentrating primarily on taking the knowledge we already have and getting it down to the local level so we actually get some change," he explains. "Partly, this means doing a better job of making local solid waste managers aware of what's possible and of providing follow-up technical assistance in selected 'targets of opportunity.' We intend, for instance, to select, by the end of this month, 10-20 localities which we feel have demonstrated a real commitment to improving their solid waste management systems (and which have asked for our help) and to go all-out to help them."

According to Hale, however, coming up with suggestions is the easy part. "What our approach also means is that we're going to have to get our message across to some groups that we haven't addressed before—the political decision-makers, state and local officials, and others who ultimately determine the kinds of solid waste management systems a locality will have. We don't intend to be content with merely submitting some recommendations and walking away, because that's only half the battle—and the easy half at that."

Even this approach, Hale admits, may take some federal money to get it going, but he vigorously maintains that such support should be small and should be the exception, rather than the rule. Hale explains, "Collection and disposal of solid wastes should be looked at as a public utility-type service, analogous to provision of water, electricity, or sewer services. It is a service provided separately, in discrete units, to individual dwelling units, for whose provision local government takes re-

### EPA: Solid waste management programs

Samuel Hale, Jr., director

H. Lanier Hickman, Jr., deputy director

John A. Hill, program development and management

#### DIVISIONS

Resource recovery—Arsen J. Darnay, Jr.

Systems management—Clyde J. Dial

Processing and disposal division—John T. Talty

#### OFFICES

State and local affairs—Ralph J. Black

Technical information—Thomas F. Williams



**EPA's Hale**

*... directing the management effort*

sponsibility. Like other utility-type services, it can (in most cases, is) and should be paid for through charges assessed against its individual users—charges which, incidentally, in most cases would be far smaller than one's electricity, water and sewer, or telephone bill."

Hale adds, "We recognize that local inertia in this area is substantial. We also feel it is very important that we prove out our approach in the next 12-15 months, and we know that selective application of limited federal funds may in many cases speed up the process of getting change. So, in addition to our technical assistance efforts, we intend to devote substantial 'planning grant' and 'demonstration grant' resources to provide limited financial assistance in selected localities where it looks like our funds could 'break a local logjam' which has prevented the locality from adopting potential nationally significant improvements."

#### **Resource recovery**

The obvious flaw with the above concept is that it applies primarily to conventional solid waste management but doesn't seem to fit resource recovery very well, yet most of the public's attention is focused on resource recovery. Hale recognizes this. "Resource recovery, which I would define to include efforts to impact on solid waste generation by attempting to influence existing product design or consumption patterns, obviously doesn't fit the approach I've described, since we're still largely exploring the unknown. Even in this area, however, we tend to look at the problem in other than

technological terms." In Hale's words, in Sections 205 and 208 of the Resource Recovery Act of 1970, the Congress said in essence that "we (Congress) think resource recovery has promise but it hasn't been adequately explored. Therefore, we direct you (EPA), first, to explore how resource recovery could be promoted and, second, to demonstrate full-scale resource recovery systems, particularly systems for recovery resources from mixed municipal wastes." EPA is devoting a substantial portion of its solid waste resources to fulfilling these two objectives.

EPA just recently announced formally, in the *Federal Register*, its first solicitation for grant proposals under Section 208, aiming to make its first Section 208 grant awards in June or July of this year. "We wrote the criteria broadly enough so that a number of diverse kinds of approaches, including energy as well as material recovery, could qualify. We also set some pretty tight technical and economic performance requirements," Hale says. Interest in these demonstrations is high, and a number of likely applicants—including the State of Delaware, working with Hercules; the City of Baltimore, which has been working with Monsanto; and Mount Vernon, NY, which recently announced its plans to apply using a system developed by Union Carbide—already have stated publicly their intentions to compete for grants under Section 208.

#### **Ongoing demonstrations**

Although it has not spent any funds under Section 208, the Office of Solid Waste Management Programs has funded other resource recovery demonstrations, most of which Hale feels are working out quite well. The first, the Franklin, OH, project (ES&T, October 1971, p 998) with the Black Clawson Co. and EPA, demonstrates the concept of hydrapulping. "In our opinion, this project has been quite successful so far, although it is far from being complete," Hale says. "We still have to resolve some tough technical and economic aspects of the operation but are most optimistic."

A second project uses straight municipal refuse and fires it as a percentage of the total input to a coal-fired boiler. "The ribbon cutting ceremony for this project will be held this month," Hale says. "This demonstration involves the city of St. Louis, in cooperation with the Union Electric Co. and EPA. The total funding for this project is \$2.4

million, with the federal contribution being more than \$1.7 million. We're excited not only about this project but about the low-capital investment requirements and broad potential applicability."

A third example of a system that the solid waste management program has funded is the CPU-400, an innovative energy recovery system of the Combustion Power Co., Menlo Park, CA (ES&T, August 1970, p 631). "The CPU has come a long way, but there are some very real technical difficulties in combustor operation and system control ahead," Hale says. "Combustion Power is still developing its pilot plant, and the prototype is years away. Their operations have been funded entirely by the federal government, some \$6 million to date. This has been a dominant proportion of EPA-sponsored resource recovery hardware-oriented projects."

#### **Major program thrusts (next 18 months)**

	(Millions of dollars)
Resource recovery where markets exist	15
Overcoming institutional barriers	
50 Local/regional planning grants	4
20 State and local demonstrations of improvements	4
Studies to promote resource recovery and improved management	3
Targeted assistance projects	2

Finally, a number of composting demonstrations have been funded. These demonstrations of composting as a resource recovery application have been worthwhile, if only for the fact that they showed that substantial economic problems are associated with composting in this country. "The technology for composting is certainly here," says Hale, but "markets and economics must improve before we will see any widespread application."

#### **Economics of resource recovery**

The other half of EPA's resource recovery efforts—finding ways to promote resource recovery—is not so visible, but Hale feels it will be ultimately more important. "People seem to forget that resource recovery is not new—it has been practiced for centuries," he says.

"There are very well-developed sec-

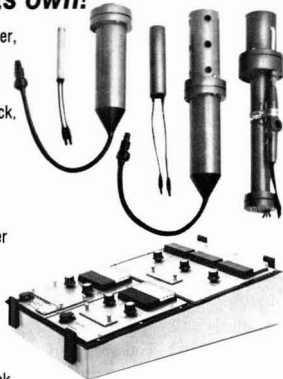
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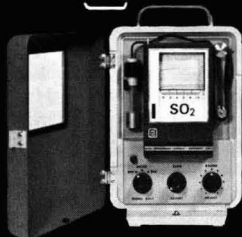
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## Tight Budget?

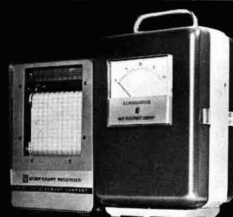
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ondary materials industries in this country," says the deputy assistant administrator. "They have existed for a long time and have been very responsive to price changes in the past. They are more capital-intensive than most people would have you believe and have made significant technological improvements in many areas. They haven't moved more strongly in the direction of resource recovery because the markets have not existed at a price at which they could cover their costs. Indeed, demand for most recovered products actually has been declining since the 1950's."

In the same vein, Hale cites the economic problems of citizen recycling centers, despite the fact they rely on essentially free labor. He also points out that, on even the most optimistic technological assumptions, most proposed municipal resource recovery systems either are not competitive with other disposal alternatives or will be competitive only if markets for recovered output can be stimulated. Thus, Hale sees markets and market prices as the major barriers to broadened resource recovery.

At the same time, EPA is looking at broad alternatives to affect these markets; it also is trying to do some things now. Freight rates are a good example. It is generally felt that freight rates discriminate against secondary materials—against ferrous scrap, for example, in favor of iron ore. "We (EPA) are pressing the freight rates issue with the Interstate Commerce Commission and other organizations," Hale says. "Import-export regulations have a lesser effect but are another area at which we're looking, as we are at materials specifications. Finally, I would like the GSA to take steps to increase the percentage of recycled materials in the products it buys."

As final evidence of his contention that Section 205 is "where the action is" in resource recovery, Hale cites the whole area of product design and consumption behavior. "We're only beginning to look at the broad possibilities for influencing generation of solid waste by trying to change patterns of production or consumption. Only efforts aimed at beverage containers have received any publicity so far, yet these efforts are quite narrow compared to, say, variable taxation of all disposable products or materials. There simply is no way to assess where this broad area will lead, but it's bound to become more important."

SSM

# Treating lead and fluoride wastes

*Westinghouse has developed a one-step process which treats wastes from TV picture tube manufacturing and leaves an effluent of drinking water quality*

All industries are faced with some sort of waste disposal problem, and the electronic tube industry is no exception. Included in the electronic tube category are color television picture tubes which produce wastes specific to their manufacture. To understand how these wastes are generated and the steps taken to prevent water pollution, color television picture tube production needs to be explained.

## TV tube production

In the first place, there is quite a difference between black and white tubes and color picture tubes. A black and white tube is one glass entity, but the color television picture tube (color cathode-ray tube) has two glass sections—a face plate and a funnel. A viewing phosphor screen of color (triads of red, green, and blue dots) is laid down on the face plate. However, this operation must take place on a clean, virgin glass surface to prevent poor registration of the color dots, imperfect dots, or contamination (when these circumstances occur, the tube is rejected).

The commonly used method to clean the face plate is light etching of the surface with hydrofluoric acid washes. After several water rinses to remove the hydrofluoric acid, phosphor dots are applied on the face plate surface by a photosensitive process with exposure through a metal aperture mask. Hydrofluoric acid is used throughout the electronic tube industry to clean, etch, and prepare all-glass envelopes prior to applying the phosphor screen.

After etching, the face plate is fused to the funnel section (and will eventually become a vacuum-sealed tube) by glass frit—a lead solder glass (70–80 wt % lead). A machine applies a fillet (bead) of frit to the edge of the funnel section. The face plate is placed on the funnel, and the combined pieces are baked in a lehr (high-temperature oven). In the lehr, solvents are driven out of the frit glass which solidifies into a solid mass and binds the two sections together.

However, if the glass does have a flaw in it or the phosphor dots are not registered properly, the picture tube assembly is rejected, salvaged, and reprocessed. To reclaim the metal mask and glass sections, the sealed tube must be taken apart.

Since the weakest point in the structure is the frit, the entire glass tube is immersed in nitric acid to weaken and dissolve the frit bond. The two glass sections are mechanically pulled apart or heat shocked (with alternate hot and cold water) to finish breaking the seal. The glass parts are then cleaned with hydrofluoric acid, and the whole process begins once more.

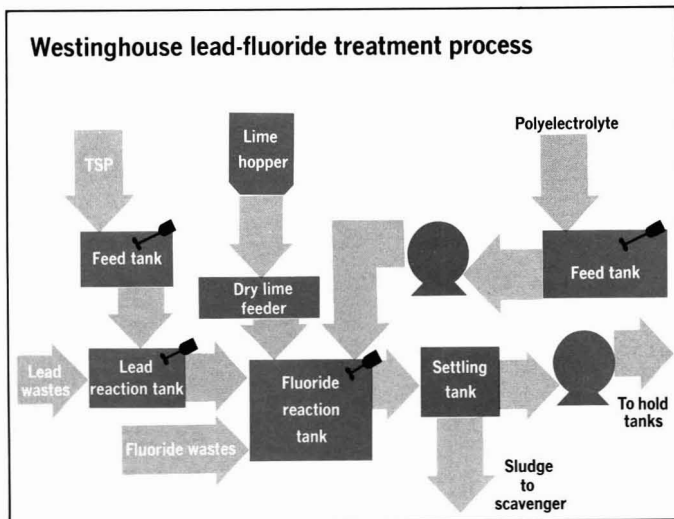
What happens to these fluoride and lead wastes that accumulate from manufacturing and reclaiming cathode-ray tubes? Westinghouse Electric Corp. (Elmira, NY) was faced with this problem. Westinghouse produces several hundred thousand tubes yearly with the resulting liquid wastes. Of the total effluent of three million gpd, 90,000 gal are lead and fluoride wastes—10,000–15,000 gal of lead wastes and the remainder is fluoride.

This indeed is a formidable amount of lead and fluoride to handle in face of the strict water quality regulations in New York State. Since the Elmira plant does not have an adjoining body of water, NY officials have classified the effluent as a discharge to groundwater. Furthermore, receiving bodies of water in the state are classified according to best usage; in this case, usage is a source of potable water supply. Discharged effluents must consequently meet state health department drinking water standards which limit lead discharges to  $1/500$  of 1 ppm and fluoride to 1.5 ppm at point of discharge.

## Treatment program

Here's how Westinghouse takes care of its lead and fluoride wastes. During the cathode-ray tube manufacturing process, the concentrated lead and fluoride wastes are individually separated from other rinse waters containing relatively small amounts of these same wastes.

Rinse waters are discharged as generated to individual collection sumps for lead and fluoride. Simultaneously, con-



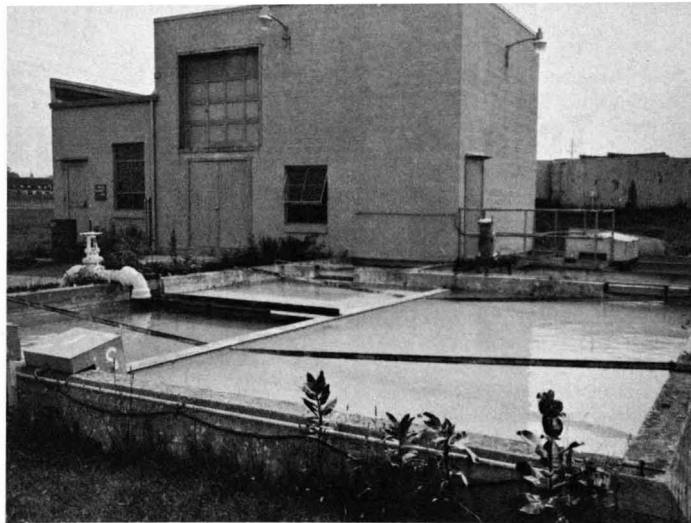
concentrated lead and fluoride wastes are continuously discharged to their collective sumps. The combined dilute and concentrated wastes then are piped to the treatment plant. Uniform concentrations of each waste are maintained by carefully metering the concentrated wastes going into the total stream.

At the treatment plant, lead wastes are fed into a tank and treated with trisodium phosphate (TSP). For best results, pH 3.6 is maintained. TSP reacts with the lead waste to precipitate lead phosphate. This treated waste, with insoluble lead in suspension, then flows into a fluoride reaction tank where the fluoride wastes are pumped in. Lime (to maintain a pH of 12) and a polyelectrolyte coagulant are added. The fluorides then precipitate as calcium fluoride.

This mixture then flows through six cascading tanks. Most of the solids are removed by settling in the first tank. The clear liquid in the last tank contains 0.2 ppm lead and 10-30 ppm fluoride which, when mixed with the remainder of Westinghouse's effluent, is within drinking water standards. Periodically, the tanks are cleaned, and the sludge (consisting of excess lime, calcium fluoride, and lead phosphate) is hauled to a landfill.

#### History

Fluoride and, in some instances, lead wastes are common to several industries: electronic tube, glass, nuclear fuel, aluminum, and fertilizer. The basic technology of the treatment process used by Westinghouse is not new. Fluoride wastes have been treated with lime, and lead wastes have been treated with phosphates and other precipitants for years. In fact, other industries routinely treat the wastes



**Disposal.** Over 90,000 gallons of lead and fluoride wastes are treated each day

separately or sometimes do not treat lead wastes at all, depending on the water quality standards of that particular region. Industries also vary fluoride waste treatment by the amounts of lime fed, pH, fluoride concentration, types of lime, retention time of the precipitate, and the mode of separation. The integrated treatment of both wastes used at Elmira is the new twist on the known technology.

During initial plant startup, Westinghouse neutralized its fluoride wastes in 55-gal drums. In the late 1950's, fluoride wastes were treated and separated by a rotary vacuum filter. The plant expanded when color television came into its own, and the vacuum filtration unit could not handle the increased volume and variety of wastes. Therefore, a continuous treatment substitute had to be found, and the present facility was completed in 1967.

All problems are not yet solved, however. More research is needed in several areas. For instance, the sludge that accumulates at the end of the treatment process eventually may have to be disposed of in ways other than landfilling (increasing numbers of landfill operations are closing as regulations tighten). In anticipation of this, Westinghouse researchers are looking into possible markets for fluoride and lead sludges.

Several patent applications have been made for converting fluoride sludges to cryolite and calcium fluoride. In fact, some aluminum firms build cryolite processing facilities adjacent to their aluminum processing plants.

Fluoride technology also has a few shortcomings. Treating fluoride wastes includes adding large amounts of lime and, in all probability, reclamation plants will not want excess lime. "We are working in the lab to develop other methods of treatment, particularly in cutting down on the lime used," says Westinghouse's Ken Rohrer, fellow engineer. Also, if a market develops for fluoride wastes, Westinghouse officials say that separate treatment may be reinstated to keep lead out of fluoride sludges.

Westinghouse officials agree that the treatment facilities are successful and efficient. The most difficult problem encountered is getting all noxious material to the treatment plant. Besides instituting employee education programs, Westinghouse has ensured that all open drains in manufacturing areas using large quantities of acids have either been closed or connected directly to the treatment plant. CKL

**Production.** Frit-sealed cathode-ray tubes are conveyed to packing stations





# WATER AND WASTE CONTROL NEWS

## Practicing the Automation we preach!

Honeywell was paying its Fort Washington (Pa.) industrial park landlord \$88,700/year to treat water and sewage from its 857,000 sq. ft. plant. At this time it was standard procedure to let water run uncontrolled through air compressors, degreasers, and plating rinse tanks, 28 of which consumed 106,700 gal./day.



**TWO-FISTED COST FIGHTER!** Two-pen ElectroniK 111 in Honeywell plant waste treatment facility records pH and Conductivity in plating department neutralizing tank. pH signal comes directly from flow-through electrode holder assembly with sensor-mounted pre-amplifier. For information on ElectroniK pH controllers write for Specification Sheets S540-2a and S546-1.

Installation of conductivity controllers on each rinse tank to measure the concentration of metallic salts so water input could be controlled, brought a 66% reduction in rinse water, to 36,260 gal./day, saving \$23,000 per year. Temperature and flow controls on the water circuit of the air compressors cut usage by \$3,000 per year. Temperature controllers to cut flow of trichloroethylene solvent cooling water saved another \$3,000 per year.

In the past three years the plant has saved one full year's water and waste treatment costs by applying the principles of good plant water management.

## "Problem-Solver" pH Electrode Better Three Ways

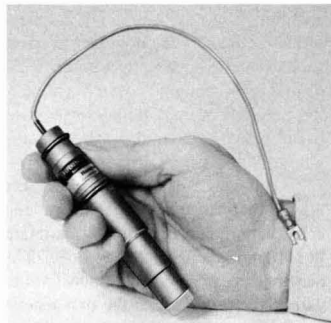
Solving three electrode problems common to process pH measurement is easy with the new Honeywell "Zero Flow" pH reference electrode.

First problem is high solution contact resistance; second is capillary clogging; and the third is "poisoning" of the silver chloride reference material by the intrusion of process fluid.

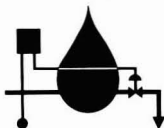
The new design develops low enough resistance to assure good contact and minimize stray effects. Large diffusion paths minimize clogging. Design licks the third problem, "poisoning", with a double-membrane, "pressure-lock" construction which places two diffusion time-constants between the process fluid and the silver chloride.

Rugged construction assures high resistance to physical and thermal shock. Ambient temperature range is -5 to 120° C. Because of its "Zero Flow" design, there's no need for accessory electrolyte reservoirs, air supplies, or pressure regulators.

For further information, write for Specification Sheet S546-1.



**pH POWER!** New Honeywell pH electrode is designed to develop low solution contact resistance, with minimum susceptibility to clogging and "poisoning".



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**NEW WATER MANAGER!** Honeywell conductivity analyzer is shown wall-mounted controlling a plating rinse tank to conserve make-up water. The submersible sensor is in the far corner of the tank. The identical equipment also is applicable to cooling tower blow-down control. Enclosures are weather-proof for hard industrial service. Also available in this line of analyzers are pH, ORP, and Dissolved Oxygen. Outputs available for ElectroniK and VutroniK recorder-controllers. For further information on analyzer transmitters write for Specification Sheets S542-1, -2, -3, and S546-1 and -2.



## Cut Costs of Plant Water Usage

"Analyzing Factors For Lower Cost Plant Water Management", a paper by Christopher P. Blakeley, develops detailed cost considerations affecting the economics of industrial plant process water usage. Blakeley, Market Manager for Honeywell Water Management Markets, presented the paper at the April 1971 meeting of the Industrial Management Center's conference on Environmental Management for Industry and Government held at Sterling Institute, Washington, D.C.

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# Wholesaling environmental services

A new agency in Maryland is a statewide utility  
that provides liquid and solid waste services

The search for environmental quality has produced few universally accepted findings. One of the few is the necessity for change—change in land use practices; change in the way we live and make our living; and change in our view of the world and man's place in it.

Nowhere have man's newly sharpened perceptions of his environment brought about more pronounced adjustments than in the rapidly shifting configuration of federal, state, and environmental agencies. Ordinarily, discussions of new governmental organizations and revised institutional structures are interesting only to those directly involved. Such actions often appear, and sometimes are, inconsequential. Yet, given the pervasive role of government in society and the magnitude of private and public effort needed to control environmental quality, it is clear that government, least of all, can afford to adopt a lethargic posture.

Most changes in environmental programs and agencies are designed to regroup existing functions and administrative units to increase their effectiveness and efficiency. Some, however, are intended to initiate new programs that differ in nature (rather than in size or structure) from previous ones. This article discusses one such agency, the Maryland Environmental Service (MES).

MES departs from the traditional state role of pollution regulator and, more recently, provider of financial assistance. The state becomes a full partner with its subdivisions and industry by providing services ranging from planning through design, financing, construction, operation, and maintenance of liquid and solid wastes treatment, reclamation, and disposal facilities.

Although it is a new type of governmental venture, the Service is not unique. Similar, though not identical, organizations are operating in New York, Ohio, and Ontario Province of Canada. MES has historical roots in river basin planning in the U.S. and other countries, notably Germany.

The agency has now been in existence for less than two years. This short time, which includes several months' gestation during which the usual budgetary and personnel matters were resolved and a staff assembled, does not justify sweeping conclusions; however, some preliminary ideas may be useful.

The simplest way to picture MES is as a statewide utility created to provide liquid and solid waste services to counties, municipalities, and industry. In order to determine how such services should be provided with both environmental protection and cost effectiveness, the Service develops liquid waste river basin plans and solid waste regional plans.

To implement plans, MES has the power to finance, manage design and construction, and operate and maintain liquid and solid waste facilities. The Service's powers and responsibilities will be discussed within the two general categories mentioned above, planning and implementation. However, this distinction is in one respect misleading—planning activities will represent the design stage of the implementation program.

## Planning

The legislation creating the Service requires that both liquid waste and solid waste planning be carried out in consultation with affected local governments, industry, and other interests.

No deadline is given for completion; however, other legislation has imposed deadlines. MES has been designated to comply on behalf of Maryland with the federal requirement that river basin plans be developed by July 1, 1973. In addition, state legislation requires each Maryland county to prepare a solid waste plan by no later than January 1, 1974. Therefore, those two dates have been set as deadlines for MES planning activities.

Federal requirements add a potential complicating factor since there will be two sets of guidelines and review procedures applied to the Service's river basin planning—one from Maryland's legislation and the other from Washington, DC.

Also, since planning for pollution abatement uses exact sciences but is not itself one, there are diverse and even conflicting views among planners and users of plans as to what constitutes the most effective methodology.

Since basin plans will require a substantial investment of money and manpower, full-scale statewide planning is being preceded by what could be considered a test plan. A small tributary of the Potomac River, the Monocacy River, is an intercounty and interstate basin and has a sufficient variety of pollution sources to require most, if not all, approaches and techniques that will be needed elsewhere in the state. A plan for this basin is nearing completion by the Service's own staff. The first draft of the plan will be circulated to agencies and individuals who will have review or implementation responsibility when all statewide basin plans are completed. If an actual plan has been produced rather than a design for the plan, there will be much better prospect for consen-

## MES state-owned facilities and project areas

Note: MES status the first of February, 1972



\* Under design or construction imminent

sus on how basin planning should be carried out. Through this device, the MES staff will have an opportunity to test various approaches and techniques before committing irretrievable time and public funds to the statewide effort.

Availability of a test or model plan will also be valuable in guiding consultants for subsequent planning, which is particularly important in light of the mix of staff and consultant resources to be employed. Although planning will continue, the magnitude of effort will decrease sharply after the initial set of basin plans has been completed. MES planning capability was designed to

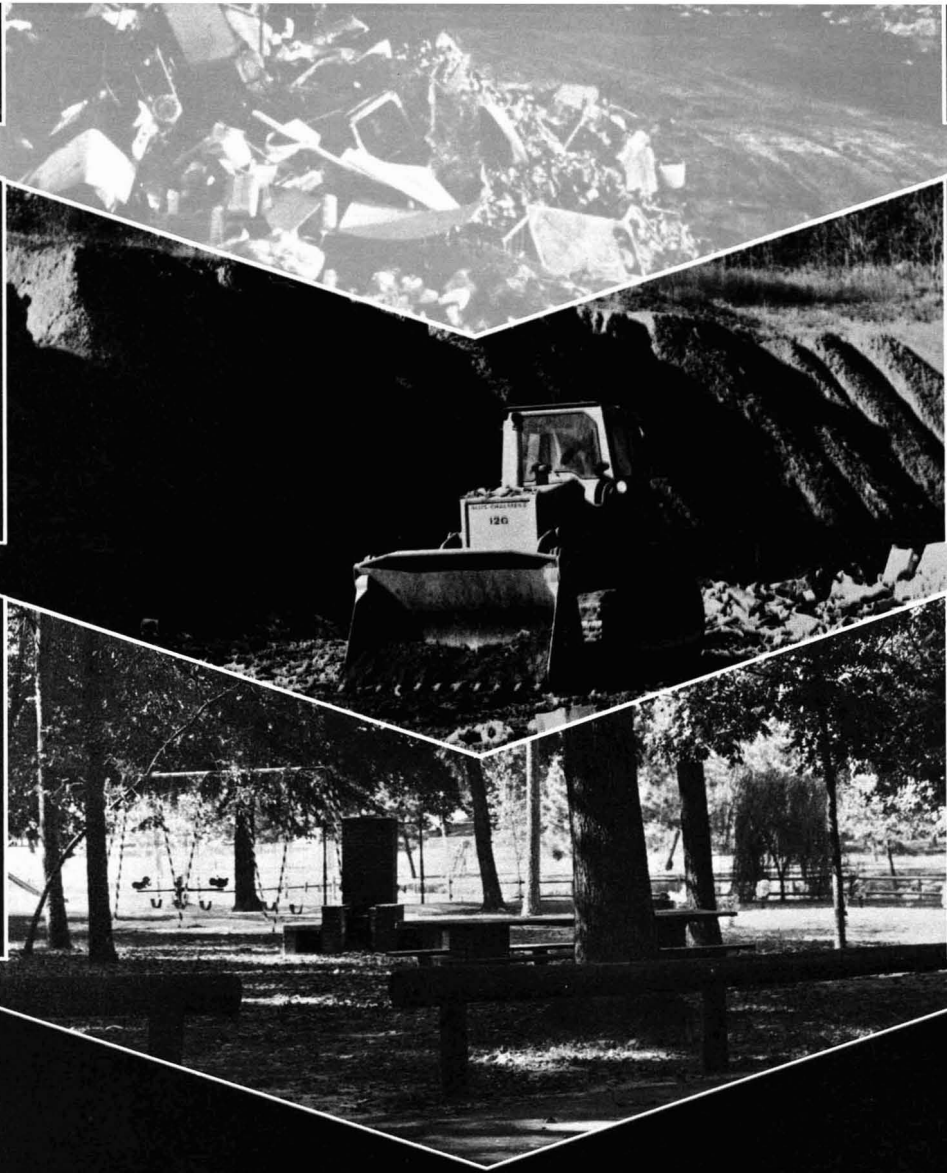
provide a maintenance planning effort subsequent to developing the initial set of plans. The difference between that capability and the capability required to develop the initial set will be made up by consultant services.

River basin planning will start from a firm foundation of existing county water supply and sewerage plans. These county plans were required by a 1966 statute—each county developed a comprehensive water supply and sewerage plan for submission and approval by the state by January 1, 1970. As expected, these plans vary in the amount of detail presented, methodology, and

quality. However, they provide an excellent inventory of problems and contain detailed schedules of actions that both counties and state are committed to take to solve existing and emerging problems.

In some measure, river basin planning will be a mechanism for improving and coordinating individual county plans. Part of the Service's planning responsibility will be a review of the county plans with three specific questions in mind:

- Are there changed circumstances that necessitate modifications? Such changes could be greater or lesser



*Metamorphosis.* MES is working to convert unsightly, unhealthy burning dumps, such as the one pictured at the top of the page, into sanitary landfills. Trash is deposited in trenches and covered with a layer of soil (second photograph) at the end of each day. Eventually, when the trench is full, the area will have recreational uses, such as parks (bottom) and golf courses.

industrialization or population growth than anticipated, revised water quality standards, or improved waste management technology.

- Are there opportunities for greater effectiveness or economy by physically combining projects proposed separately within a county or within two or more counties?

- Are there similar opportunities to provide regional management of waste facilities, even though those facilities might not be physically interconnected?

Basin plans will identify physical projects or other actions needed to provide adequate waste management. Approval of the plan by both state and affected local jurisdictions will constitute a commitment on their part to implement all measures called for. The plan will also specify responsibilities for taking actions; for example, whether a given sewage treatment plant is to be constructed and operated by a local government or by MES. The Service's own enabling act requires that plans contain

a five-year work schedule. The planning horizon will be longer, but details and commitments will be more generalized beyond the five-year time period specified by law. Plans are subject to biennial review and amendment as circumstances warrant.

#### **Solid waste planning**

Solid waste planning is being carried out on a somewhat different basis. As stated earlier, both counties and MES were simultaneously given responsibility

for solid waste planning—on a county by county basis by local government and on a regional basis by the Service. Requirements of both legislative acts could be carried out by having the 24 major subdivisions of Maryland (23 counties and Baltimore City, which is considered a county in this context) and MES separately pursue their solid waste planning activity. At best, this action would waste money and effort and almost certainly produce two conflicting sets of solid waste plans. Therefore, MES has entered into contract negotiation with the counties to agree on joint solid waste planning. In most, if not all, areas of the state, counties and MES will jointly fund and direct a solid waste planning effort which will satisfy statutory requirements for both regional and individual county plans. Whether a regional plan is looked on as a compilation of coordinated individual county plans or whether the individual county plans are considered as components of a larger regional plan is immaterial, just as long as the planning effort is organized and directed properly. Since MES will be an active participant in solid waste planning, the state itself will be a planning region.

Regional planning boundaries can assume more importance than they warrant. As indicated, MES will be active throughout the state. For purposes of technical analysis, hydrologically defined areas, economic regions, geographic provinces, and similar areas have more importance than political boundaries; however, political boundaries are important in reviewing and adopting plans. Therefore, technical planning will be guided by many factors other than political boundaries whereas the liaison, coordination, and review activities leading to adopted plans will be carried out with political boundaries being kept uppermost in mind.

When the initial set of solid waste and river basin plans are completed, data, information, action schedules, and other elements of statewide planning can be placed in any desired format—whether that be a single county, a multi-county area, an economic region, or any other defined geographical area. It will not be equally simple to coordinate the planning within the state boundary with that of adjacent states. Before each specific planning project is undertaken, close working relationships will be established with appropriate authorities within the adjacent state. Since Maryland is a small state, virtually every

plan, regardless of its object or geographic orientation, will have interstate aspects.

### Implementation

As indicated, planning responsibility was assigned to MES to provide an orderly means for determining physical projects that the Service should undertake. In the long run, the planning device is expected to, and undoubtedly will, be the principal route for establishing Service projects. However, there are two other ways by which MES may construct and operate a waste management facility—a “mandatory response to a request” and a “response to a directive.”

The law provides that any governmental entity or privately owned concern within Maryland may request the Service to provide liquid or solid waste services. MES is obligated to provide such services. The only two negotiable items are the date for initiating such services and the rate that will be charged. If rates are not agreed on by negotiation, the Maryland Public Service Commission is empowered to provide binding arbitration.

The reason for the “mandatory response to requests” provision in the law is to remove temptation for MES to pick and choose among the needs existing within the state and concentrate exclusively on those which were financially attractive or environmentally glamorous. The provision also ensures local government and industry that they will receive uniform treatment from the Service. This uniformity does not extend to rates since these must reflect operation costs which will vary from place to place and from time to time.

The “response to directive” provision stipulates that MES can be used as an implementing arm of the regulatory authority of the state. If either the Secretary of Health and Mental Hygiene or the Secretary of Natural Resources, both of whom have pollution control regulatory responsibility, determines that a pollution abatement order has not been met with compliance, he may direct the Service to take whatever action is required to ensure compliance with the order. This provision is intended to be used in instances where imminent hazard to public health or natural resources exists and is not or cannot be resolved by responsible local authorities or individuals. It also expresses the state's commitment to use its powers wherever and whenever needed to

abate pollution if other responsible authorities are unable to do so.

Even though MES is still initiating its planning program, efforts are nevertheless under way to develop specific physical projects to prevent delays in solving existing problems. The State and Federal Water Pollution Control Construction Grant Program and intensified enforcement of solid waste disposal laws and regulations have greatly accelerated construction of sewage treatment plants, sanitary landfills, and related facilities. When the Service was created, officials realized that some important decisions were about to be made on constructing waste facilities which represented a large investment of public funds and would have a long-range constraining influence on possible future waste management systems. In some instances, the Service's abilities and powers to develop joint undertakings between municipalities, counties, and private industry could be incorporated to improve proposed systems. Therefore, several problem areas in Maryland have been selected for intensive study, even though not yet part of any regional solid waste or river basin planning activity. At this time, it is impossible to say how many of these studies will result in contracts and physical projects; however, the fact that they have been undertaken will at least assure local, state, and federal governments involved that possible alternatives to decisions are examined while still relevant.

Among such possible projects is a sewage treatment plant which would replace one proposed local plant and four existing plants that are scheduled for replacement, upgrading, or expansion into a single regional plant. Another, which is now under contract, will result in a sewage treatment plant to provide urgently needed services to a community and replace two nearby inadequate plants serving public institutions. Other projects under consideration have to do with solid waste and sewage sludge problems which have become extremely serious in the urban areas of the state. The accompanying map and tables indicate the scope of present investigations and project development activities.

The Service will cut its operating teeth on facilities serving state institutions. In response to an Executive Order of Governor Marvin Mandel, MES is presently operating 14 state-owned sewage treatment plants, supervising

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**Expansion.** To update sewage treatment, MES may enlarge inadequate facilities

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### Advantages

Reasons for creating MES and the promise that it holds for the future are exemplified in these proposals. One of the hallmarks of most of them is that they deal with more than one local jurisdiction. In one instance, the jurisdictions are widely separated. This ability to act as an agent on behalf of a number of individual entities, whether they be political subdivisions or commercial enterprises, or some combination of the two categories, is in itself a significant and essential element of an effective waste management system. This applies not only to the ability to bring together two jurisdictions with similar problems, but also to bring together two separate jurisdictions when one may possess the solution to the other's problem. For example, organic solids, removed during sewage treatment are expensive and unwanted wastes so far as the owner of the sewage treatment plant is concerned. However, areas with barren soils or scarred landscapes would benefit from proper application of those solids if properly processed. Although formidable technical, economic, and political obstacles are encountered in transporting materials which are a "waste" at their place of origin but could be a resource to some other jurisdiction, there is reason to hope that such proposals will gain public acceptance when proved to be sound. The existence of an agency which has equal responsibility to both the jurisdiction that generates waste and the one which may offer to receive it should be valuable for accepting such projects in the future.

Another advantage of MES is that it offers the small community opportunities to achieve economies of scale which are usually available only to the larger

cities. This is true not only in construction but also in operations. For example, it has become increasingly necessary to provide small communities with high-performance treatment plants in order to achieve water quality standards. Such plants, even when small, are usually complex and require operating skills, competent laboratory support, and ready availability of spare parts and emergency equipment comparable in quality to those required at large plants. All of these resources are quite expensive for the small community and are, therefore, rarely provided adequately. MES can greatly alleviate such problems by providing regional management of several such small plants. In this fashion, a highly skilled (and therefore, well-paid) operator/supervisor could be available, as well as a centralized laboratory and emergency equipment stocks. Such centralized regional management would also provide economies in purchasing supplies and equipment and should provide greater reliability.

Economies of scale in operation and construction are important now in solid waste disposal and may well become even more important as reclamation replaces disposal. Availability of a regional management system may be essential if wastes are to be collected and transported to central reclamation and recycling centers.

Even before regional reclamation facilities become available, regional collecting and processing of specific kinds of solid waste may be desirable. For example, MES is studying statewide collection for reprocessing or safe disposal of waste oils, tires, paper, fly ash, and waste sludges. Another study, with a somewhat different orientation, will deal with toxic materials and hazardous substances. Many of these materials are handled poorly, if at all, on a local basis but would lend themselves to a regional or statewide effort.

Another advantage of the Service is the ability to provide centralized and highly specialized resources which individual jurisdictions cannot normally provide themselves. These resources include such planning tools as mathematical models and such operating tools as computerized operation and maintenance scheduling.

Although many advantages offered by the Service result from the ability to centralize facilities and management systems, safeguards are built into the law to protect local autonomy. The most important of these is a prohibition against MES determining who shall receive solid and liquid waste services and who shall not. If the Service could make such decisions, it would replace or at least weaken the position of local government as the land use authority. The Service acts only as a wholesale agency, which can provide financing, construction, and operation of liquid or solid waste reclamation or disposal facilities, but it cannot decide what properties will be served by collection facilities. Its rates, of course, will reflect both volume and characteristics of collected wastes and provide an economic feedback to the community making land use decisions. This, however, is the same kind of economic feedback that the community would have or at least should have if it operated the plant itself.

Another safeguard protecting local autonomy and land use decisions is a requirement that MES plans be predicated on implementing land use plans of local jurisdictions. MES cannot revise the local land use plan to make waste management cheaper. Again, as in the case of rate structure, a solid waste and river basin plan will serve as a feedback to local government on its land use plan, but the principle must be retained that waste management planning must specify hardware and actions to implement land use planning rather than control it.

#### Funding

Several sources of funds are available to support the Services activities: general appropriations, bond sales, revenues, and grants. With the exception of planning costs, all of the Service's activities are to be self-supporting. Providing liquid or solid waste services must be supported by a contract specifying that all costs (debt service, operations, and administrative overhead) are to be met by charges to the political or commercial entity receiving the service. MES is empowered to sell its own bonds, secured

principally by revenues and backed by power to divert state-local shared revenues as well as a reserve fund.

MES could not become self-supporting until a substantial number of revenue-producing projects were in operation. Therefore, general appropriations were made available initially to organize the agency, and will continue to be needed at decreasing levels for the next few years.

Costs of developing the initial set of plans is being met by a special \$4 million general obligation bond authorization. No revenues, of course, will be available to defray these costs.

To date the prospects for success are excellent. Substantial time and effort have been and will continue to be required to promote better understanding and acceptance of the agency and assistance it can offer. There is a natural indication, on the part of local government in particular, to look on MES as just another regulatory agency. There is also a predictable concern by local governments over becoming captives of the state without adequate control to protect their interests in matters relating to charges and rate structures.

However, substantial progress has been made in alleviating these concerns and in gaining acceptance of the mission of MES. There is every reason to believe that within a short time the Maryland Environmental Service and the concepts it embodies will be accepted not only as a valid approach but as the principal approach to achieve effective waste management and control of environmental quality.



*Thomas D. McKewen is presently director of the Maryland Environmental Service. He has worked with the State of Maryland since 1952 in areas dealing with sanitary engineering, public water supply, water and sewerage, resource protection, and environmental health services. Mr. McKewen has been director of MES since 1970.*

# new



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## Mathematical Model for Fate of Pollutants in Near-Shore Waters

Walter J. Wnek and Edward G. Fochtman<sup>1</sup>

IIT Research Institute, 10 W. 35th St., Chicago, IL 60616

Mathematical concepts necessary to calculate the fate of pollutants in the near-shore waters of a lake are developed and an example calculation involving three separate sources calculated. The model considers variable diffusion coefficients and variable velocities. Use of transforms and Green's function avoids the finite differences approach, permits rapid calculation, and results in a stable answer for long distances from the source.

Lake Michigan has long been used as a means for disposal of sewage and industrial waste. There is a clear need to reverse the trend of deteriorating water quality and to preserve this valuable resource. Recent efforts to abate pollution have focused attention on the complex nature of the problem and the lack of reliable information on the fate and persistence of pollutants introduced into the lake. Such information is needed to direct antipollution efforts rationally so that those steps can be taken that will result in the greatest effect for their cost.

While many scientists have studied this problem on both an experimental and theoretical basis, there is still a great need for more definitive predictive techniques. In this work, available mathematical techniques were modified to develop a program which requires little computer time and is more amenable to prediction of conditions at greater distances or times from the source. Effects of multiple sources, boundaries, and reaction or decay rates were also considered.

### Qualitative Description of Model

At the beginning of the study, possible dispersion mechanisms were selected, and consequences of these evaluated—e.g., molecular diffusion, velocity gradients, and turbulence. The mechanism which provided the best explanation of the dispersal process was one based on the concept of dispersion as an eddy diffusion process. Although phenomena of the diffusion type have been observed in many other fields, differences in these fields from pollution of Lake Michigan were great enough so that developments in them could not directly be taken and applied to the process of dispersion in a lake.

The equation based on this concept, which governs distribution of a pollutant, is given by the partial differential equation:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} + v_z \frac{\partial c}{\partial z} = \frac{\partial}{\partial x} \left( K_x \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial c}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_z \frac{\partial c}{\partial z} \right) - R(c) \quad (1)$$

subject to the initial condition

$$c(x,y,z,0) = 0$$

and the boundary condition of no mass flux across the bounding surface  $S$

$$\frac{\partial c}{\partial n} = 0 \text{ on } S$$

where  $c$  is concentration;  $x,y,z$  are coordinates measured respectively in the direction of the shore, across the lake, and vertically downward (Figure 1);  $t$  is time;  $n$  is normal to  $S$ ;  $v_x, v_y,$  and  $v_z$  are velocities for the  $x,y,z$  directions, respectively, functions of  $x,y,z$ ;  $K_x, K_y, K_z$  are turbulent dispersion coefficients for  $x,y,z$  directions respectively, functions of  $x,y,z$ ; and  $R$  is rate of reaction of pollutant with its environment.

This equation is arrived at by performing a material balance on a differential element of volume anywhere in the lake.

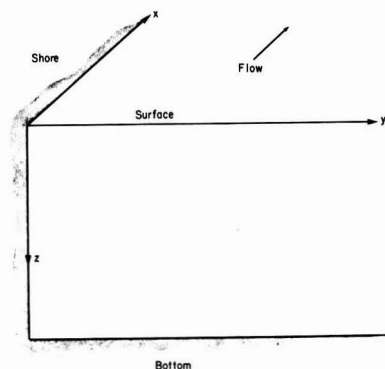


Figure 1. Diagram of coordinate system for Lake Michigan

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First term represents local time rate of change of concentration, the next three terms define changes in concentration due to advection, the next three terms account for dispersive action of the pollutant due to turbulence, and the last term allows for depletion of the pollutant due to chemical reaction with its environment.

Although several analytical solutions to Equation 1 are available in the literature (Crank, 1957; Carslaw and Jaeger, 1959), they could not be used owing to the simplifying assumptions made, such as constant dispersion coefficients and velocities, no reaction term, no boundaries, and a two-dimensional coordinate system. Another method used to solve Equation 1 is to use a numerical technique such as finite differences (Water Resource Engineers, 1966; 1968a,b). Unfortunately, this method of solution requires tremendous computer time and tends to be unstable for predictions far in the future.

It was possible to remove these stringent restrictions and reduce the computation time to a few seconds by developing an analytical solution by particular transformations and the concept of Green's functions. The model of Lake Michigan can calculate the amount of pollution due to any number of sources on the lake at any time and point in the shore waters of the lake. The dispersion coefficients, velocities, and reaction term can be arbitrary functions. The model also allows for boundaries such as the lake's bottom and shoreline, thermoclines, and thermobars.

An expanded description of the model and its development along with an example problem are presented.

#### Quantitative Description of Model

**Correlations for Eddy Diffusion Coefficients.** Eddy diffusion coefficients are characteristic parameters of a given lake and are empirically determined. Although few experimental values have been determined (FWPCA, 1967) for the Great Lakes, enough data have been taken on other bodies of water such as rivers (Glover, 1964), oceans (Hill, 1966; Koczy, 1958; Ozmidov, 1958; Foxworthy and Kneeling, 1969) and other lakes (Hutchinson, 1957) so that order-of-magnitude estimates can be made from the following correlations.

Longitudinal dispersion means dispersion in the direction of flow. It includes the combined action of turbulence and variation of velocity with position. Glover (1964) gives data expressed as eddy diffusion coefficients for rivers which can be used to account for turbulence due to shear flow. Diffusivity in longitudinal direction due to flow in the  $x$  direction is

$$K_{x0} \text{ (ft}^2/\text{sec)} = c_{Kx} R_H v^*$$

A similar formula for transverse dispersion is

$$K_{y0} \text{ (ft}^2/\text{sec)} = c_{Ky} R_H v^*$$

and for vertical dispersion

$$K_z \text{ (ft}^2/\text{sec)} = c_{Kz} H v^*$$

where

$c_{Kx}$ ,  $c_{Ky}$ ,  $c_{Kz}$  = empirical constants for a given body of water whose values are approximately 500, 0.72, and 0.067, respectively [see Glover (1964) for further details]

$$v^* \text{ (ft/sec)} = \sqrt{g v_z / N_c} \text{ (shear velocity)}$$

$g$  = gravitational constant

$v_z$  (ft/sec) = inshore velocity in  $x$  direction

$$N_c = 1.49 R_H^{0.167} / N_m \text{ (Chezy coefficient)}$$

$$R_H \text{ (ft)} = HL/2(H + L) \text{ (hydraulic radius)}$$

$$H \text{ (ft)} = \text{depth of lake or thermocline}$$

$$L \text{ (ft)} = \text{width of lake or thermobar}$$

$$N_m = \text{Manning's constant} \sim 0.025$$

Similar formulas apply for flow in the  $y$  and  $z$  directions. To account for the variation of these eddy diffusion coefficients with distance due to transition from small to large eddy motions inherent in homogeneous turbulence, the following correlations from the oceanography literature (Hill, 1966) may be used. The longitudinal and transverse coefficients decrease with depth according to:

$$\frac{\Delta K_x / \Delta z}{K_x |_{\text{surface}}} \text{ or } \frac{\Delta K_y / \Delta z}{K_y |_{\text{surface}}} = -\alpha \text{ (Hill, 1966; FWPCA, 1967)}$$

where

$$\alpha \cong 4.6 \times 10^{-3} \text{ ft}^{-1}$$

Longitudinal and transverse coefficients on the surface increase with distance from the source up to the length scale of large eddy motion (Hill, 1966; Ozmidov, 1958)

$$K_x |_{\text{surface}} = c_x r^{4/3}$$

$$K_y |_{\text{surface}} = c_y r^{4/3}$$

where  $r$  (ft) =  $\sqrt{x^2 + y^2}$  is the absolute distance from the source and

$$1 \times 10^{-4} \leq c_s \leq 2.5 \times 10^{-3} \text{ ft}^{2/3}/\text{sec}$$

For Lake Michigan, this length scale is about 800 ft so that for distances greater than 800 ft, diffusivities do not vary (FWPCA, 1967). Combining these relationships, the expressions for the eddy diffusion coefficients as functions of the three space variables are

$$K_x = K_{x0} + c_x r^{4/3} (1 - \alpha z)$$

$$K_y = K_{y0} + c_y r^{4/3} (1 - \alpha z)$$

$$K_z = c_{Kz} H v^*$$

For values of  $r$  greater than 800 ft,  $r$  should be set equal to 800.

Although the model can include flows in more than one direction, these coefficients include only velocity in the  $x$  direction, along the shore. The effect of shear is incorporated in  $K_x$  so that  $K_x$  should be larger than  $K_y$  and  $K_z$ , since the latter include only the effect of turbulence. To get a feeling of the magnitude of these diffusivities, let us calculate them under the following conditions:

$$z = 20 \text{ ft}$$

$$r > 800 \text{ ft}$$

$$H = 27 \text{ ft}$$

$$v_x = 0.072 \text{ ft/sec}$$

The value of the Chezy coefficient and the shear velocity are

$$N_c = \frac{1.49(27)^{0.167}}{0.025} = 104$$

$$v^* = \frac{\sqrt{32.2}(0.072)}{104} = 3.82 \times 10^{-3}$$

so that

$$K_{x0} = 500(27)(3.82 \times 10^{-3}) = 51.5$$

$$K_{y0} = 0.72(27)(3.82 \times 10^{-3}) = 0.074$$

$$K_z = 0.067(20)(3.82 \times 10^{-3}) = 5.1 \times 10^{-3}$$

Values of the diffusivities are then

$$\begin{aligned} K_x &= 51.5 + 2.5 \times 10^{-3}(800)^{4/3}(1 - 4.6 \times 10^{-3} \times 20) \\ &= 51.5 + 16.6 = 68.1 \text{ ft}^2/\text{sec} \\ K_y &= 0.074 + 16.6 = 16.7 \text{ ft}^2/\text{sec} \\ K_z &= 5.1 \times 10^{-3} \text{ ft}^2/\text{sec} \end{aligned}$$

One may compare these values with radial diffusivity measured for Lakes Michigan and Erie which is a combination of  $K_x$  and  $K_y$  (Table I). Correlations for  $K_x$  and  $K_y$  are seen to be in agreement with the data. Although there is no equivalent data for  $K_z$ , its correlation has been confirmed by numerous measurements on rivers (Glover, 1964) and is in agreement with ocean data (Koczy, 1958).

**Modification and Solution of the General Equation for Lake Michigan. FORM OF RATE EQUATION.** Experimentally, it has been found that for several nonconservative materials introduced in the lake such as BOD,  $R(c)$  is best represented by a first-order reaction term as

$$R(c) = kc \quad (2)$$

where  $k$  is a constant having units 1/time and is on the order of 0.1/day and that the velocities and dispersion coefficients are only functions of the coordinates and not concentration. Using these facts, it is seen that Equation 1 is simplified to a second-order linear partial differential equation for which an analytical solution appears feasible.

By rearranging Equation 1, making two changes of variables, and using separation of variables, Equation 1 can be further simplified so that an analytical solution can be obtained by means of the method of Green's functions.

**REDUCTION TO THE CONSTANT COEFFICIENT EQUATION WITH A MODIFIED SOURCE TERM.** Let mean velocities and diffusivities be defined as:

$$\bar{v}_i = \frac{1}{v_p} \int_{x_0}^{x_p} \int_{y_0}^{y_p} \int_{z_0}^{z_p} v_i(x', y', z') dx' dy' dz' \quad i = 1, 2, 3 \quad (3a)$$

$$\bar{K}_i = \frac{1}{v_p} \int_{x_0}^{x_p} \int_{y_0}^{y_p} \int_{z_0}^{z_p} K_i(x', y', z') dx' dy' dz' \quad i = 1, 2, 3 \quad (3b)$$

where  $i = 1, 2, 3$  represents  $x, y, z$ . The subscripts 0 and  $P$  denote the source and the point where concentration is desired, respectively.  $v_p$  is the volume element equal to  $(x_p - x_0)(y_p - y_0)(z_p - z_0)$ .

Introducing these quantities into Equation 1 yields the constant coefficient equation

$$\frac{\partial c}{\partial t} + \sum_{i=1}^3 \bar{v}_i \frac{\partial c}{\partial x_i} = \sum_{i=1}^3 \bar{K}_i \frac{\partial^2 c}{\partial x_i^2} + S(c, \mathbf{x}) \quad (4)$$

where

$$S(c, \mathbf{x}) = \sum_{i=1}^3 (\bar{v}_i - v_i) \frac{\partial c}{\partial x_i} + \frac{\partial}{\partial x_i} \left[ (K_i - \bar{K}_i) \frac{\partial c}{\partial x_i} \right]$$

and is to be treated as a source term. The rationale behind this is that the solution for an arbitrary source term can be readily written in terms of the solution for an instantaneous point source which is designated as the Green's function. It should be noted that  $S$  is a measure of the deviation of the true solution from that for the mean coefficient case. For this reason,  $S$  can be considered as perturbing the mean coefficient solution.

**ANALYSIS OF CONVECTION TERMS.** Make the following change of variables.

$$\hat{x} = x - \bar{v}_x t \quad (5a)$$

$$\hat{y} = y - \bar{v}_y t \quad (5b)$$

**Table I. Experimental Values of the Radial Diffusivity  $K_r$  for Lakes Michigan and Erie (FWPCA, Lake Michigan Currents, 1967)**

Depth, ft	$z$ , ft	$v$ , ft/sec	$K_r$ , ft <sup>2</sup> /sec
27	20	0.098	31.2
27	5	0.111	59.1
27	20	0.072	39.8
25	5	0.101	44.2
42	20	0.066	34.4
42	20	0.098	35.5

$$\hat{z} = z - \bar{v}_z t \quad (5c)$$

Then

$$\frac{\partial c}{\partial x_i} = \frac{\partial c}{\partial \hat{x}_i} \quad i = 1, 2, 3 \quad (6)$$

and

$$\frac{\partial^2 c}{\partial x_i^2} = \frac{\partial^2 c}{\partial \hat{x}_i^2} \quad (7)$$

Also

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial t} + \sum_{i=1}^3 \frac{\partial c}{\partial \hat{x}_i} \frac{\partial \hat{x}_i}{\partial t} = \frac{\partial c}{\partial t} - \sum \bar{v}_i \frac{\partial c}{\partial \hat{x}_i} \quad (8)$$

Substituting Equations 5-8 into Equation 4

$$\frac{\partial c}{\partial t} = \sum_{i=1}^3 \bar{K}_i \frac{\partial^2 c}{\partial \hat{x}_i^2} - kc + S(c, \hat{\mathbf{x}}, t) \quad (9)$$

**ANALYSIS OF DIFFUSION TERMS.** Make the following change of variables:

$$X_i = \frac{\hat{x}_i}{\sqrt{\bar{K}_i}} \quad i = 1, 2, 3$$

Then

$$\frac{\partial^2 c}{\partial \hat{x}_i^2} = \frac{1}{K_i} \frac{\partial^2 c}{\partial X_i^2} \quad (10)$$

Substituting Equation 10 into Equation 9

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial X^2} + \frac{\partial^2 c}{\partial Y^2} + \frac{\partial^2 c}{\partial Z^2} - kc + S(c, \mathbf{X}, t) \quad (11)$$

**SIMPLIFYING TRANSFORMATION IN TERMS OF THE RATE CONSTANT.** Let

$$c = e^{-kt} \hat{c} \quad (12)$$

Then, substituting Equation 12 into Equation 11

$$\frac{\partial \hat{c}}{\partial t} = \frac{\partial^2 \hat{c}}{\partial X^2} + \frac{\partial^2 \hat{c}}{\partial Y^2} + \frac{\partial^2 \hat{c}}{\partial Z^2} + e^{kt} S(\hat{c}, \mathbf{X}, t) \quad (13)$$

This equation is now in the form of the simple diffusion equation, and the methods available for solving it can be used. The solution for an instantaneous point source will be found from which the solution for an arbitrary source term can be generated.

**SEPARATION OF VARIABLES.** Assuming a solution of the form

$$\hat{c} = f_1(X, t) f_2(Y, t) f_3(Z, t) \quad (14)$$

and substituting it into Equation 13 without the source term

$$f_2 f_3 \left( \frac{\partial f_1}{\partial t} - \frac{\partial^2 f_1}{\partial X^2} \right) + f_1 f_3 \left( \frac{\partial f_2}{\partial t} - \frac{\partial^2 f_2}{\partial Y^2} \right) + f_1 f_2 \left( \frac{\partial f_3}{\partial t} - \frac{\partial^2 f_3}{\partial Z^2} \right) = 0$$

Since  $(f_1, f_2, f_3) \neq (0, 0, 0)$ , then

$$\frac{\partial f_1}{\partial t} = \frac{\partial^2 f_1}{\partial X^2} \quad (15a)$$

$$\frac{\partial f_2}{\partial t} = \frac{\partial^2 f_2}{\partial Y^2} \quad (15b)$$

$$\frac{\partial f_3}{\partial t} = \frac{\partial^2 f_3}{\partial Z^2} \quad (15c)$$

TRANSIENT SOLUTION FOR A POINT SOURCE. A solution of Equation 15 is

$$f_i = \frac{A}{t^{1/2}} \exp[-(X_i^2/4t)] \quad (16)$$

where  $A$  is an arbitrary constant.

Substituting Equation 16 into Equation 14

$$\hat{c} = \frac{A}{t^{3/2}} \exp[-(X^2/4t) - (Y^2/4t) - (Z^2/4t)] \quad (17)$$

Substituting Equation 17 into Equation 12

$$c = \frac{Ae^{-kt}}{t^{3/2}} \exp[-(X^2/4t) - (Y^2/4t) - (Z^2/4t)] \quad (18)$$

Transforming back to the  $\hat{x}, \hat{y}, \hat{z}$  coordinate system, Equation 18 becomes

$$c = \frac{Ae^{-kt}}{t^{3/2}} \exp \left\{ - \left[ \left( \frac{\hat{x}}{\sqrt{K_x}} \right)^2 / 4t \right] - \left[ \left( \frac{\hat{y}}{\sqrt{K_y}} \right)^2 / 4t \right] - \left[ \left( \frac{\hat{z}}{\sqrt{K_z}} \right)^2 / 4t \right] \right\} \quad (19)$$

or

$$c = \frac{Ae^{-kt}}{t^{3/2}} \exp[-(\hat{x}^2/4K_x t) - (\hat{y}^2/4K_y t) - (\hat{z}^2/4K_z t)] \quad (20)$$

Transforming back to the  $x, y, z, t$  coordinate system, Equation 20 becomes

$$c = \frac{Ae^{-kt}}{t^{3/2}} \exp[-(x - \bar{v}_x t)^2/4K_x t - (y - \bar{v}_y t)^2/4K_y t - (z - \bar{v}_z t)^2/4K_z t] \quad (21)$$

The constant  $A$  depends on the boundary conditions. To obtain the Green's function, the boundary condition is selected as an instantaneous point source of amount  $M$  at  $(0, 0, 0)$ . Later, provision is made for sources not on the shore.

With the reaction term  $k = 0$ , the following relation holds

$$M = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} c|_{k=0} dx dy dz \quad (22)$$

which states that the amount of material released must be contained somewhere in the system if no reaction occurs. Substituting Equation 21 into Equation 22, integrating, and solving for  $A$  (Crank, 1957)

$$A = \frac{M}{8(\pi t)^{3/2} \sqrt{K_x K_y K_z}}$$

Therefore, the solution for an instantaneous source is

$$c = \frac{Me^{-kt}}{8(\pi t)^{3/2} \sqrt{K_x K_y K_z}} \exp[-(x - \bar{v}_x t)^2/4K_x t - (y - \bar{v}_y t)^2/4K_y t - (z - \bar{v}_z t)^2/4K_z t] \quad (23)$$

The Green's function is the solution for a unit instantaneous point source released at  $x', y', z', t'$  and no decay. Thus,

$$G(x, y, z, t; x', y', z', t') = \frac{1}{8[\pi(t-t')]^{3/2} \sqrt{K_x K_y K_z}} \times \exp \left\{ - \frac{[(x-x') - \bar{v}_x(t-t')]^2}{4K_x(t-t')} - \frac{[(y-y') - \bar{v}_y(t-t')]^2}{4K_y(t-t')} - \frac{[(z-z') - \bar{v}_z(t-t')]^2}{4K_z(t-t')} \right\} \quad (24)$$

TRANSIENT SOLUTION FOR A CONTINUOUS SOURCE. The solution for an arbitrary source is obtained from the solution for the instantaneous source by integrating it over instantaneous sources released every  $dt$ . However, it will be convenient first to rearrange Equation 23.

Let

$$a = \frac{\bar{v}_x K_x x^2 + \bar{v}_y K_y y^2 + \bar{v}_z K_z z^2}{4K_x K_y K_z}$$

$$b = \bar{v}_x^2/4K_x + \bar{v}_y^2/4K_y + \bar{v}_z^2/4K_z + k$$

Then

$$c = \frac{M}{8(\pi t)^{3/2} \sqrt{K_x K_y K_z}} \exp \left( \frac{x\bar{v}_x}{2K_x} + \frac{y\bar{v}_y}{2K_y} + \frac{z\bar{v}_z}{2K_z} \right) \times \exp \left( - \frac{a}{t} - bt \right) \quad (25)$$

Let the pollutant be introduced at rate  $\varphi(\xi)$  into the lake continuously at  $(0, 0, 0)$  where  $\xi$  is the time of introduction. Then the effect of a quantity of pollutant  $\varphi d\xi$  on concentration at the point  $x, y, z$  at time  $t$  is given by

$$c = \frac{\varphi \exp \left( \sum_{i=1}^3 \frac{x_i \bar{v}_i}{2K_i} \right)}{8\pi^{3/2} \sqrt{K_x K_y K_z}} \int_0^t \varphi(\xi) \times \exp \left[ - \frac{a}{t-\xi} - b(t-\xi) \right] \frac{d\xi}{(t-\xi)^{3/2}} \quad (26)$$

If the rate  $\varphi$  is taken as a constant or a suitable mean value, then

$$c = \frac{\varphi \exp \left( \sum_{i=1}^3 \frac{x_i \bar{v}_i}{2K_i} \right)}{8\pi^{3/2} \sqrt{K_x K_y K_z}} \int_0^t \frac{\exp \left[ - \frac{a}{t-\xi} - b(t-\xi) \right]}{(t-\xi)^{3/2}} d\xi \quad (27)$$

$$\text{Let } u = \sqrt{\frac{a}{(t-\xi)}}$$

$$\beta = ab$$

Then  $du = 1/2 u^3/ad\xi$  and Equation 27 becomes

$$c = \frac{2\varphi \exp \left( \sum_{i=1}^3 \frac{x_i \bar{v}_i}{2K_i} \right)}{8\pi^{3/2} \sqrt{aK_x K_y K_z}} \int_{\sqrt{a/t}}^{\infty} \exp \left( -u^2 - \frac{\beta}{u^2} \right) du \quad (28)$$

The integral in Equation 28 has been evaluated (Abramowitz and Stegun, 1965) so that Equation 28 becomes

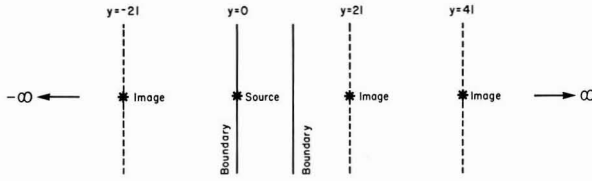


Figure 2. Pictorial representation of the method of images

$$c = \frac{\varphi \exp\left(\frac{x\bar{v}_x}{2\bar{K}_x} + \frac{y\bar{v}_y}{2\bar{K}_y} + \frac{z\bar{v}_z}{2\bar{K}_z}\right)}{16\pi\sqrt{a\bar{K}_x\bar{K}_y\bar{K}_z}} \times \left\{ \exp(2\sqrt{\beta}) \left[ 1 - \operatorname{erf}\left(\sqrt{\frac{a}{t}} - \sqrt{\frac{\beta t}{a}}\right) \right] + \exp(-2\sqrt{\beta}) \left[ 1 - \operatorname{erf}\left(\sqrt{\frac{a}{t}} + \sqrt{\frac{\beta t}{a}}\right) \right] \right\}$$

where

$$\operatorname{erf}(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\eta \exp(-w^2) dw \quad (29)$$

For a continuous source released at  $t = t_0$  at  $x = x_0, y = y_0, z = z_0$ , Equation 29 should be modified by the substitution

$$x = x - x_0, \quad y = y - y_0, \quad z = z - z_0, \quad t = t - t_0$$

STEADY-STATE SOLUTION FOR A CONTINUOUS SOURCE. To obtain the steady-state solution, take the limit of Equation 28 as  $t \rightarrow \infty$  to obtain

$$c = \frac{\varphi \exp\left(\frac{x\bar{v}_x}{2\bar{K}_x} + \frac{y\bar{v}_y}{2\bar{K}_y} + \frac{z\bar{v}_z}{2\bar{K}_z} - 2\sqrt{\beta}\right)}{8\pi\sqrt{a\bar{K}_x\bar{K}_y\bar{K}_z}} \quad (30)$$

CORRECTION DUE TO THE NONCONSTANT COEFFICIENTS. If the term  $e^{kt}S$  in Equation 13 is considered as a source distributed over the space and time domains, then a first-order correction may be applied to the solution for the case of mean coefficients by adding the term

$$\Delta c = e^{-kt} \int_0^t dt' \int_0^\infty \int_0^\infty \int_{-\infty}^\infty \times e^{k t' t} S(c, \mathbf{x}', t') G(\mathbf{x}, t; \mathbf{x}', t') dx' dy' dz'$$

where  $c$  is the solution for the case of mean coefficients. In general, this integral must be evaluated numerically. However, since the velocities and diffusivities are not strong functions of position and the solutions are not extremely sensitive with respect to them, the corrections would not be expected to be a great amount.

FINITE BOUNDARIES. To account for finite boundaries (such as the surface and bottom of the lake, a thermocline, the shorelines, or a thermobar), the procedure is as follows: If the pollutant is of the type that deposits on the bottom such as suspended solids, so that the boundaries are absorbing ones, the previous solutions may be used. However, if it is reflected at the boundaries as dissolved solids are, then the condition that there is no flow of pollutant across these boundaries must be satisfied. These conditions for rectangular boundaries are expressible as

$$\begin{aligned} \bar{v}_z c - \bar{K}_z \frac{\partial c}{\partial z} &= 0 & \text{at } z = 0 \text{ and } z = l_1 \\ \bar{v}_y c - \bar{K}_y \frac{\partial c}{\partial y} &= 0 & \text{at } y = 0 \text{ and } y = l_2 \end{aligned} \quad (31)$$

and can be satisfied if the concentration profile for an infinite system is considered to be reflected first at  $z = l_1$ , again at  $z = 0$ , then at  $x = l_1$  and so on, then at  $y = l_2$ , again at  $y = 0$ , then at  $y = l_2$ , and so on with the result of each successive reflection being superimposed on the original profile. This will produce a double infinite series for the concentration profile in a finite system. An equivalent approach to this problem is to use the method of images in which an infinite system of sources is placed outside of the finite system such that their fluxes cancel at the boundaries. In addition, the velocity field for the images is replaced by the negative of that for the source for those components not parallel to the boundary.

To show that this method does indeed give zero flux at the boundaries, let us evaluate the flux at  $y = 0$  for the simple case of an instantaneous point source at  $x = 0, y = y_0, z = 0$  and a reflecting boundary at  $y = 0$ . Only one image source at  $y = -y_0$  with a negative velocity in the  $y$  direction is required. Using Equation 23, the concentration is

$$c = \frac{2Me^{-kt}}{8(\pi t)^{3/2}\sqrt{\bar{K}_x\bar{K}_y\bar{K}_z}} \exp\left[-\frac{(x-\bar{v}_x t)^2}{4\bar{K}_x t} - \frac{(z-\bar{v}_z t)^2}{4\bar{K}_z t}\right] \times \left\{ \exp\left[-\frac{(y-y_0-\bar{v}_y t)^2}{4\bar{K}_y t}\right] + \exp\left[-\frac{(y+y_0+\bar{v}_y t)^2}{4\bar{K}_y t}\right] \right\}$$

so that the flux is

$$\begin{aligned} \bar{v}_y c - \bar{K}_y \frac{\partial c}{\partial y} &= \frac{2Me^{-kt}}{8(\pi t)^{3/2}\sqrt{\bar{K}_x\bar{K}_y\bar{K}_z}} \times \\ &\exp\left[-\frac{(x-\bar{v}_x t)^2}{4\bar{K}_x t} - \frac{(z-\bar{v}_z t)^2}{4\bar{K}_z t}\right] \left\{ \left[ \bar{v}_y + \frac{2(y-y_0-\bar{v}_y t)}{4\bar{K}_y t} \right] \times \right. \\ &\exp\left[-\frac{(y-y_0-\bar{v}_y t)^2}{4\bar{K}_y t}\right] + \left[ -\bar{v}_y + \frac{2(y+y_0+\bar{v}_y t)}{4\bar{K}_y t} \right] \times \\ &\left. \exp\left[-\frac{(y+y_0+\bar{v}_y t)^2}{4\bar{K}_y t}\right] \right\} \end{aligned}$$

Substituting  $y = 0$

$$\begin{aligned} \left( \bar{v}_y c - \bar{K}_y \frac{\partial c}{\partial y} \right)_{y=0} &= \frac{2Me^{-kt}}{8(\pi t)^{3/2}\sqrt{\bar{K}_x\bar{K}_y\bar{K}_z}} \times \\ &\exp\left[-\frac{(x-\bar{v}_x t)^2}{4\bar{K}_x t} - \frac{(z-\bar{v}_z t)^2}{4\bar{K}_z t}\right] \left\{ \left[ \bar{v}_y - \frac{(y_0+\bar{v}_y t)}{2\bar{K}_y t} \right] \times \right. \\ &\exp\left[-\frac{(y_0+\bar{v}_y t)^2}{4\bar{K}_y t}\right] - \left[ \bar{v}_y - \frac{(y_0+\bar{v}_y t)}{2\bar{K}_y t} \right] \times \\ &\left. \exp\left[-\frac{(y_0+\bar{v}_y t)^2}{4\bar{K}_y t}\right] \right\} \equiv 0 \end{aligned}$$

Before applying these methods to the problem at hand, let us further demonstrate the method for the problem of a source at  $y = 0$  in a one-dimensional medium with boundaries at  $y = 0$  and  $y = l$ . If  $f(y, t)$  is the solution for the semi-infinite case, then it can be seen from Figure 2 that the solution for the finite case is

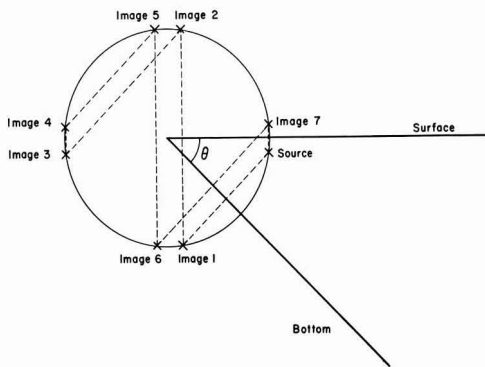


Figure 3. Location of images for a sloping bottom

$$\sum_{n=-\infty}^{\infty} f(z - 2nl)$$

where the velocity field for the images is the negative of that for the source, and the summation starts at  $n = 0$  and progresses  $1, -1, 2, -2, \dots, +n, -n$ .

Thus, the solution for the finite case satisfying the boundary conditions expressed by Equation 31 for a source located at  $(x_0, y_0, z_0)$  and released at  $t_0$  may be written down as

$$C(x, y, z, t) = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \times \{ c[x - x_0, y + (2ml_2 - y_0), z + (2nl_1 - z_0), t - t_0] + c[x - x_0, y + (2ml_2 - y_0), z + (2nl_1 + z_0), t - t_0] + c[x - x_0, y + (2ml_2 + y_0), z + (2nl_1 - z_0), t - t_0] + c[x - x_0, y + (2ml_2 + y_0), z + (2nl_1 + z_0), t - t_0] \} \quad (32)$$

where the negative of  $\bar{v}_y$  is to be used for images in the  $y$  direction and the negative of  $\bar{v}_z$  for images in the  $z$  direction.  $C$  can be either Equation 23 for the instantaneous source case, Equation 29 for the transient continuous source case, or Equation 30 for the steady-state continuous source case.

Another example of the use of image sources is the case of a sloping bottom as shown in Figure 3. The reasoning behind the system of images shown is as follows: Image 1 cancels the flux due to the source across the bottom; image 2 cancels the flux due to image 1 across the surface; image 3 cancels the

flux due to image 2 across the bottom, etc. As shown in Carslaw and Jaeger, 1959, if  $\theta = \pi/m$  where  $m$  is a positive integer, the  $2m$ th image will coincide with the source so that a closed system is obtained.

**MULTIPLE SOURCES.** To treat multiple sources, one calculates the contribution for each source as given by Equation 32 and adds them to obtain the combined effect. This is justified because the general partial differential equation is linear.

#### Example Problem

It is desired to know the individual and combined effects of three outfalls situated on the shoreline of Lake Michigan on the concentration of BOD along the shoreline and 50 ft out from shore.

Locations, concentrations of BOD, and flow rates of the three outfalls are:

- Outfall 1:  $x = 0$ , 20 ppm, 10,000 gpm
- Outfall 2:  $x = 2000$  ft, 50 ppm, 50,000 gpm
- Outfall 3:  $x = 5000$  ft, 30 ppm, 200,000 gpm

During the time of year to be considered, velocity along the shore of the lake is 1 ft/sec, mean depth is 30 ft, and there is a thermobar 500 ft offshore. The rate constant for the decomposition of BOD is 0.1 day.

Information to be obtained are: (1) the steady-state contribution of each outfall to the BOD and their total for  $y = 0$  and  $y = 50$  ft from  $x = -5000$  ft to  $x = 20,000$  at 1000 ft increments, and (2) concentration history due to outfalls at the shoreline 5000 ft downstream for outfall 3.

**Solution:** The requested information is given in graphical form in Figures 4-6. They were obtained for the conditions: (1) reflecting boundaries at  $y = 0$  and 500 ft and at  $z = 0$  and  $z = 30$  ft; (2)  $v_x = 1$  ft/sec,  $v_y = v_z = 0$ ; and (3) mean diffusivities using the same parameters as in the sample calculation.

#### Nomenclature

- $c$  = concentration
- $c_{K_x}, c_{K_y}, c_{K_z}$  = empirical constants, dimensionless
- $c_s$  = empirical constant,  $\text{ft}^{2/3}/\text{sec}$
- $g$  = gravitational constant
- $H$  = depth, ft
- $k$  = first-order rate constant,  $\text{sec}^{-1}$
- $K_x, K_y, K_z$  = turbulent dispersion coefficients for the  $x, y, z$  directions, respectively,  $\text{ft}^2/\text{sec}$
- $K_{x_0}, K_{y_0}$  = turbulent dispersion coefficients due to shear for the  $x, y$  directions, respectively,  $\text{ft}^2/\text{sec}$

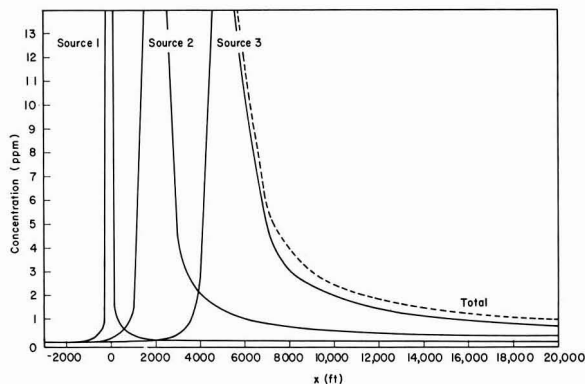


Figure 4. Concentration of BOD along shoreline for  $y = z = 0$  at steady state

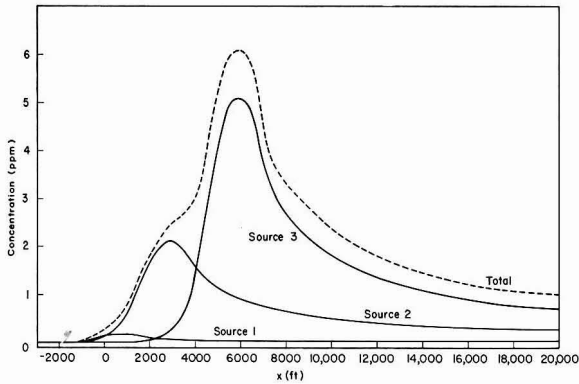


Figure 5. Concentration of BOD along shoreline for  $y = 50$  ft and  $z = 0$  at steady state

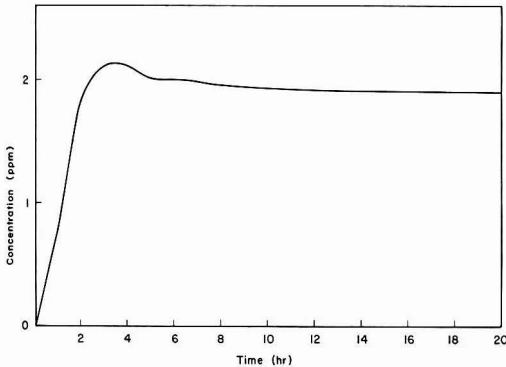


Figure 6. Transient concentration of BOD at shoreline due to source 3 5000 ft downstream from source 3

- $L$  = width, ft
- $n$  = normal to  $S$
- $N_c$  = Chezy coefficient
- $N_m$  = Manning's constant
- $r$  =  $\sqrt{x^2 + y^2}$ , ft
- $R$  = rate of reaction of pollutant with its environment
- $R_H$  = hydraulic radius, ft
- $S$  = bounding surface
- $t$  = time, sec
- $v^*$  = shear velocity, ft/sec
- $v_x, v_y, v_z$  = velocities for the  $x, y, z$  directions, respectively, ft/sec
- $x$  = coordinate measured in direction of shore, ft
- $y$  = coordinate measured in direction across lake, ft
- $z$  = coordinate measured in direction vertically downward, ft
- $\alpha$  = empirical constant,  $\text{ft}^{-1}$

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# Variations of Sulfur Isotope Ratios in Samples of Water and Air Near Chicago

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■ Sulfur-34 variations were measured in surface waters, municipal wells, sewage treatment plants, rain, and air in a suburban area west of Chicago. The study was centered on Salt Creek which, with neighboring streams, apparently characterizes the glacial-deposit area as being depleted in <sup>34</sup>S, with respect to meteoritic troilite. Three apparent perturbants of <sup>34</sup>S enrichment in the small stream were rain, earth-surface disturbances, and effluents from sewage treatment plants. Deep municipal wells (>350 meters) were strongly enriched in <sup>34</sup>S and shallow municipal wells (<85 meters) were strongly depleted. Enrichment in rain varied as widely during single storms as from storm to storm. The average enrichment in atmospheric SO<sub>2</sub> and sulfate particulate matter was essentially equivalent to that of rain.

Current interests in the world budget of sulfur and its relation to environmental pollution, as implied by Robinson and Robbins (1970) and by Morgan et al. (1970), give importance to analytical methods that can be useful in the assessment and control of sulfur-related pollution. The mass spectrometric measurement of <sup>34</sup>S enrichments in environmental water and air is such a method, and it has been in recent use by investigators studying the atmosphere, rain, and groundwater systems. Research groups at Brookhaven National Laboratory (Tucker, 1969) and Dequasie and Grey (1970) applied it to the examination of the atmosphere; Cortecci and Longinelli (1970), Mizutani and Rafter (1969), and Ostlund (1959) applied it to rain samples; Longinelli and Cortecci (1970), Postgate (1968), Horowitz et al. (1969), and Melpar (1970) used sulfur isotope ratios in studies of surface-water systems.

According to a recent estimate by Thode (1970) on the distribution of sulfur isotopes in nature, evaporite minerals are generally enriched in <sup>34</sup>S, relative to meteoritic troilite, and sedimentary minerals are generally depleted. Fossil fuels vary over a wide range depending on differing geological histories. Seawater sulfate has a uniform enrichment of about 20 ppt.

Enrichments in atmospheric precipitation may be expected to depend on natural and industrial sources of SO<sub>2</sub> and particulate sulfates; enrichments in surface-water systems should depend on atmospheric precipitation and on the ground media through which rainwater percolates before accumulating in streams and wells.

This paper reports measurements of <sup>34</sup>S enrichments in the sulfates of surface-water systems, wells, sewage treatment plant effluents, rain, and air in a suburban area of Chicago. The data were gathered for the purpose of looking for patterns

of isotopic distribution, applicable to the study of pollution in the vicinity of a large city.

The main part of the study was focused on the drainage basin of Salt Creek which is a sluggish stream flowing through some of the western suburbs of Chicago. The basin has an area of about 150 sq miles and a topography that was originally fixed by the deposition of glacial debris. The unconsolidated glacial deposits almost completely cover the bedrock throughout the region of the basin and in some areas extend to depths of about 200 ft.

In addition to Salt Creek and its tributaries, municipal wells and sewage treatment plants of the Salt Creek Basin were sampled and analyzed for <sup>34</sup>S enrichment. A few other streams in northern Illinois were analyzed, including Little Vermillion River which is comparable in size to Salt Creek but is located in a farming region midway between Lake Michigan and the Mississippi River. Samples from Lake Michigan and from 13 peripheral streams flowing into the lake were examined. Other materials analyzed for <sup>34</sup>S enrichment were air and rain (sampled in the western suburban area of Chicago), randomly selected household detergents, and a few samples of seawater.

## Experimental

The sulfates of all water samples were precipitated as BaSO<sub>4</sub> by conventional procedures. The BaSO<sub>4</sub> was filtered, washed free of chlorides, ignited at 800°C, and weighed for measurement of sulfate concentration. About 20 mg of the BaSO<sub>4</sub> was converted to SO<sub>2</sub> by a thermal decomposition procedure reported by Holt and Engelkemeir (1970). An important precaution for this procedure, not reported previously, is that the quartz surfaces on which the decomposition of BaSO<sub>4</sub> occurs should be free of organic contamination (fingerprints, paper fibers, dust, etc.); such can contribute to the mass-50 peak in subsequent mass spectrometric analysis. This precaution is accomplished by preignition of the quartz reaction tubes, quartz capsules, quartz powder, and quartz wool. The preignited capsules are then handled only with clean forceps.

Atmospheric SO<sub>2</sub> and particulate sulfate were collected on paper filters that were pretreated with a solution of 25% K<sub>2</sub>CO<sub>3</sub> and 10% glycerol, according to the procedure of Huygen (1963). After passing about 100 m<sup>3</sup> of air through each filter, it was boiled in water, to which bromine water had been added, to convert all of the collected sulfur compounds to sulfate for subsequent precipitation as BaSO<sub>4</sub>.

The SO<sub>2</sub> obtained from the pyrolysis of BaSO<sub>4</sub> was analyzed on a high-precision, dual-collector, isotope-ratio mass spectrometer (Model NAA-RM57, Nuclide Analysis Associates, State College, PA).

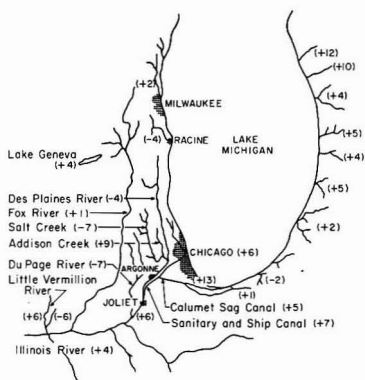
The <sup>34</sup>S enrichment of each sample with respect to a secondary standard (a tank of SO<sub>2</sub>, +3.6 ± 0.3 ppt with respect to Canyon Diablo meteoritic troilite) was calculated from the two measured ratios 66/64 and 50/48, referred to below as *R*<sup>66</sup> and *R*<sup>50</sup>, respectively. These ratios relate to the isotope ratios of <sup>34</sup>S and <sup>18</sup>O by Equations 1 and 2

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**Table I. Sulfate Concentrations and <sup>34</sup>S Enrichments in Municipal Wells and Sewage Treatment Plants**

Municipality	Date	Well water (untreated)			Sewage plant effluent		
		Depth, m	SO <sub>4</sub> , mg/l.	δ <sup>34</sup> S <sub>C.D.</sub> , ppt	Date	SO <sub>4</sub> , mg/l.	δ <sup>34</sup> S <sub>C.D.</sub> , ppt
Hinsdale	8/14/70	85	293	-13.4			
Addison	8/14/70	47	238	-14.2	8/4/70	205	-8.6
Wood Dale	8/14/70	75	170	-7.2	8/4/70	220	-2.8
Elmhurst	8/14/70	427	83	+24.2	8/4/70	113	+11.2
Oak Brook	8/14/70	457	87	+22.3	8/4/70	156	+8.6
Western Springs	4/1/70	366	111	+21.9			
Joliet	9/8/70	518	114	+18.0	9/8/70	148	+7.8
Villa Park		>350			8/4/70	126	+9.8



**Figure 1. <sup>34</sup>S enrichments in surface-water systems near Chicago**

$$R^{66} = R^{34} + R^{18} \quad (1)$$

$$R^{50} = R^{34} + 1/2 R^{18} \quad (2)$$

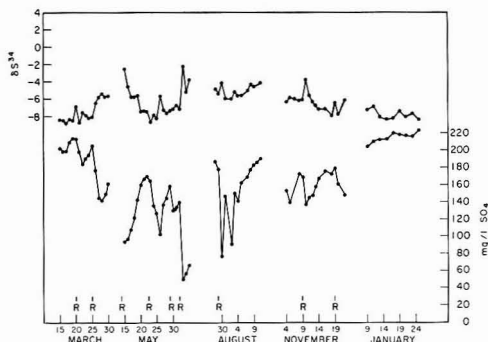
Equations 1 and 2 are combined and substituted in Equation 3 to give the <sup>34</sup>S enrichment of a sample (x) with respect to a standard (std), δ<sup>34</sup>S, in ppt, corrected for <sup>18</sup>O contribution,

$$\delta^{34}S, \text{ ppt} = \left[ \frac{R_x^{34} - R_{std}^{34}}{R_{std}^{34}} \right] 1000 = \left[ \frac{2 R_x^{50} - R_x^{66}}{2 R_{std}^{50} - R_{std}^{66}} - 1 \right] 1000 \quad (3)$$

Results are reported with respect to Canyon Diablo meteoritic troilite, δ<sup>-34</sup>S<sub>C.D.</sub>. The standard deviation obtained on four separate conversions of a single supply of BaSO<sub>4</sub> was ±0.2 ppt.

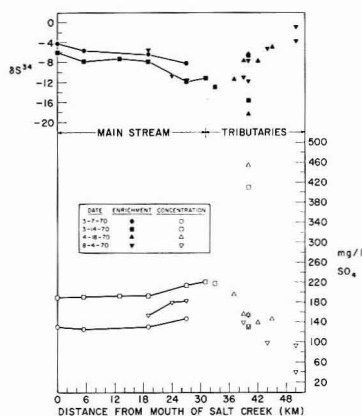
**Results and Discussion**

<sup>34</sup>S enrichments for surface waters are shown on the map in Figure 1. These are averaged values for 105 measurements on Salt Creek, eight for Addison Creek, five for Des Plaines River, five for DuPage River, two for Fox River, six for Little Vermillion River, four for Lake Michigan, two for Chicago Sanitary and Ship Canal, and two for Calumet Sag Canal; single values for Lake Geneva, Illinois River, and each of the small rivers flowing into Lake Michigan. Daily variations in Salt Creek are plotted in Figure 2, and variations with distance from the mouth of the stream are plotted in Figure 3. Results obtained on nearby municipal wells and sewage treatment plants are given in Table I. Variations in sequential samples of



**Figure 2. Daily variations of sulfate concentration and <sup>34</sup>S enrichment of Salt Creek at the Graue Mill sampling station**

R denotes rain or melting snow



**Figure 3. Variations of sulfate concentration and <sup>34</sup>S enrichment with distance along Salt Creek**

rain in two storms are shown in Figure 4, and results on composite samples from a series of storms are shown in Figure 5. Results on a series of atmospheric air samples are plotted in Figure 6. Figure 7 summarizes most of the data gathered in this investigation.

**Salt Creek and Other Nearby Surface Waters.** The average <sup>34</sup>S enrichment values shown in Figure 1 indicate that Salt Creek and the nearest neighboring streams (except Addison

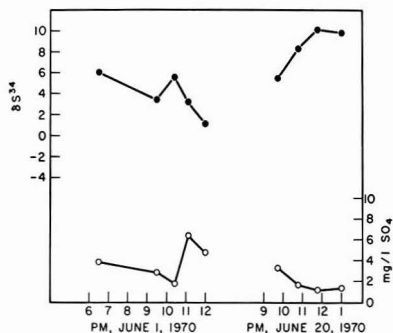


Figure 4. Variations of sulfate concentration and  $^{34}\text{S}$  enrichment in rain during two storms at Hinsdale

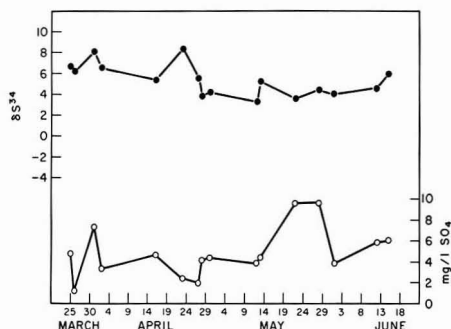


Figure 5. Variations of sulfate concentration and  $^{34}\text{S}$  enrichment in composite rain samples of sequential storms at Argonne, March-June 1970

Creek) are characteristically negative. The  $-7$  ppt for Salt Creek,  $-7$  ppt for DuPage River,  $-4$  ppt for Des Plaines River and  $-4$  ppt for the small stream at Racine, WI, suggest that the soil of the region drained by these streams is characteristically depleted in  $^{34}\text{S}$ . The exceptional, strongly positive enrichment of Addison Creek ( $+9$  ppt), the largest tributary of Salt Creek flowing through a central section of the region, will be discussed later.

Lake Michigan and the shipping canals that drain some of its water into the Illinois River are about  $+6$  ppt with respect to sulfur in meteoritic troilite. In view of basic studies, such as by Nakai and Jensen (1964), the sulfates remaining in a large body of water like Lake Michigan may be expected to be enriched in the heavier sulfur isotope as a result of fractionation that accompanies bacterial reduction of sulfates to insoluble sulfides.

**Time Variations of Enrichment and Sulfate Concentration in Salt Creek.** The data plotted in Figure 2 shows general inverse variation between  $^{34}\text{S}$  enrichment and concentration of dissolved sulfates at a single sampling station. Each abrupt dilution of the stream (av  $-7$  ppt) by rain or melting snow (av  $+5$  ppt) was usually accompanied by an increase in  $^{34}\text{S}$  enrichment. The effect appeared to be less pronounced in August when a flood followed a mild drought. During this abnormal condition, the enrichment remained at a relatively high level, while the concentration at the sampling site appeared to oscillate from day to day, possibly due to a cyclic pattern of temporary storage and drainage of flood waters

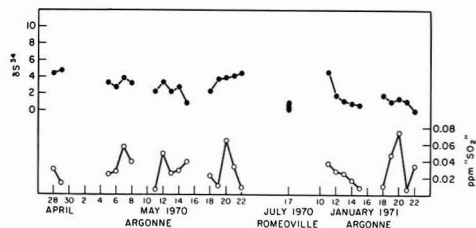


Figure 6. Concentration and  $^{34}\text{S}$  enrichment of  $\text{SO}_2$  and particulate sulfates in air samples collected at Argonne and Romeoville

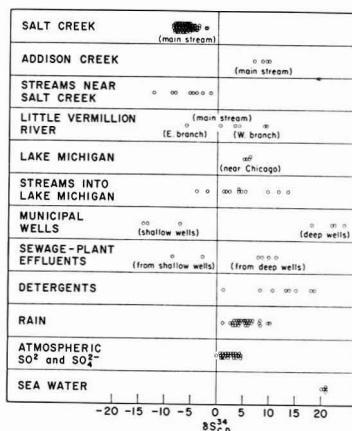


Figure 7. Summary of  $^{34}\text{S}$  data

within low areas upstream. In general, the  $^{34}\text{S}$  enrichment was higher in the summer than in the winter.

**Variations with Distance along Salt Creek.** The  $^{34}\text{S}$  enrichment also tended to vary inversely with sulfate concentration along the expanse of the stream on various sampling dates (Figure 3). Two factors that appeared to contribute to this condition were: earth-surface disturbances (such as open mine drainage and highway construction), which tended to increase concentration and decrease enrichment; and discharge from a sewage plant which tended to lower concentration and increase enrichment.

Heavy road construction was in progress in the vicinity of about 33–40 km from the mouth of Salt Creek; Figure 3 shows this to be the region of increasing concentration and decreasing enrichment. The two sets of extreme values at about 40 km ( $411$  mg/l. and  $-16$  ppt on 3/14/70;  $455$  mg/l. and  $-18$  ppt on 4/18/70) were obtained on samples taken downstream from an inactive gravel mine into which the stream drained and then was removed by mechanical pumps. A few weeks later, when the stream was diverted around the mine, the enrichment and concentration values returned to levels that were near normal for the area ( $155$  mg/l. and  $-12$  ppt). The observed effects of earth-surface disturbances (road construction and exposed gravel mines) suggest that the deeper glacial deposits, which have not been leached by percolation of rainwater as much as have surface soils, contain sulfates of more negative  $^{34}\text{S}$  than is ordinarily present in the creek.

The two branches of the Little Vermillion River, a stream

comparable in size to Salt Creek but not urbanized, differed widely (east branch, -6 ppt; average west branch, +6 ppt) on the day of sampling (see Figures 1 and 7). A quarry was in operation on the east branch, and it may have been a source of relatively high concentrations of sulfate that was depleted in  $^{34}\text{S}$ . The enrichment of the main stream (0.5 ppt) was a resultant of the two branches.

Figure 3 indicates that another perturbation of the  $^{34}\text{S}$  enrichment of Salt Creek apparently occurred at a point about 23 km from the mouth. The enrichment was higher in samples taken downstream from this point on three different sampling dates. The sewage treatment plants of two large suburbs, Elmhurst and Villa Park, are located in this vicinity, and, as will be pointed out in the next section, both plants discharge sewage effluents that are highly enriched in  $^{34}\text{S}$  (+11 ppt and +10 ppt, respectively).

Addison Creek, although the largest tributary of Salt Creek, is a relatively small stream flowing through some highly industrialized suburbs. A large sewage plant near its head discharges water that originates from deep wells (ca. 450 meters) in Bensenville. The deep-well water, which in this area appears to be characteristically strongly enriched, apparently renders the entire stream distinctly positive (+9 ppt), even though the surrounding streams are distinctly negative (Figures 1 and 7).

**Municipal Wells and Sewage Treatment Plants.** The data in Table I indicate that the municipal wells 85 meters or less in depth were strongly depleted in  $^{34}\text{S}$  (-7 to -14 ppt) and the wells 350 meters or more in depth were strongly enriched (+18 to +24 ppt). The shallower wells draw water from upper aquifers in strata of dolomite and overlying glacial deposits; the deep wells draw from a lower aquifer in sandstone and dolomite strata. The sulfur-isotope analyses indicate that, according to Thode (1970) and others, the deposits of the upper aquifer may be sedimentary and those of the lower aquifer may contain evaporites. The comparative data of Table I reveal that the  $^{34}\text{S}$  enrichments of sewage-plant effluents correspond to the wells from which they are fed. Enriched deep wells produce enriched sewage plant effluents and depleted shallow wells produce depleted sewage plant effluents, albeit the enrichment or depletion is substantially attenuated by isotope diluents such as rain and household (and/or industrial) wastes. Analyses of some randomly selected household detergents are included in Figure 7 for comparison.

The discharges of sewage plant effluents into Salt Creek, and particularly into Addison Creek, as noted above, apparently had pronounced effects upon the  $^{34}\text{S}$  enrichments of these streams.

**Rain and Air.** Sequential samples of rainwater were collected from two storms at suburban Hinsdale. The data plotted in Figure 4 show that the variations in  $^{34}\text{S}$  enrichment during each of these storms (+6 ppt to +1 ppt and +5 ppt to +10 ppt) were as great as the entire range of variations in several total-storm samples (+3 ppt to +8 ppt), collected

at the Argonne meteorology station, Figure 5. A comparison of the concentration and enrichment data obtained on the storm of 6/1/70, Figure 4, suggests that a change in concentration of sulfate in the rainwater lagged by an hour or so a change in  $^{34}\text{S}$  enrichment, which, presumably, was caused by a shift in meteorological conditions. All of the experimental data obtained on rain (av. ca. +5 ppt) are given in Figure 7.

Figure 6 shows some day-to-day variations of  $^{34}\text{S}$  enrichment in air samples, collected at Argonne in April and May of 1970 and in January 1971. Also included are values obtained 7/17/70 on five air samples collected by aircraft flying through the plume of a major fossil fuel power plant at Romeoville, six miles southwest of Argonne. The average enrichment value for all of the analyzed air samples (+2 ppt) was very close to the average for rain in the same area (+5 ppt).

#### *Acknowledgment*

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# Photochemistry of Atmospheric Samples in Los Angeles

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■ During the fall of 1968, samples of downtown Los Angeles air were collected in large plastic bags and irradiated with natural sunlight. The samples were analyzed periodically before and during irradiation for C<sub>1</sub> to C<sub>10</sub> hydrocarbons, nitric oxide, NO<sub>2</sub>, peroxyacetyl nitrate (PAN), total oxidant, and CO. The reactivities of the samples were calculated, and the effects of sunlight intensity, temperature, and sample composition on reactivity were evaluated. Correlation of the rates of reaction of the individual hydrocarbons of these samples with rates reported for irradiated synthetic mixtures provides a validation of the irradiation chamber technique for studying atmospheric photochemistry. The samples, which were collected during morning traffic, closely resembled diluted auto exhaust mixed with light paraffins from natural gas and gasoline evaporative losses. There was a wide variation in uv light dosage from day to day with a resulting strong effect on degree of atmospheric reactivity and associated pollution manifestations. The effects of uv dosage were also studied by attenuating the sunlight with a screen.

Although much information has been collected on irradiation of synthetic mixtures of pollutants and of auto exhaust, few studies have been reported on irradiation of samples of polluted air.

Stephens and Scott (1962) reported on the sunlight irradiation of three air samples taken on a freeway near central Los Angeles. They found that propylene and the terminal butenes reacted more rapidly than ethylene. Concentrations of acetylene and the paraffins remained unchanged, although the samples were irradiated for up to 18 hr.

Stephens and Burleson (1967) collected air samples in 20-l. glass carboys at Riverside, CA, and irradiated them for 24 hr with Blacklite fluorescent lamps. A 50% loss of ethylene occurred in 8 hr and a 75% loss in 24 hr of irradiation. Losses of the most reactive paraffins (*n*-hexane, cyclopentane, *n*-pentane, and isopentane) were 70–80% of the ethylene losses. Acetylene loss was approximately 15% in 24 hr, and even ethane showed a slight loss in two of three samples studied.

Altshuller et al. (1968, 1970) collected some atmospheric samples in Los Angeles in plastic bags and irradiated them with sunlight. Measurements of propylene and isobutylene showed half-lives of 3½ hr, and the concentration of *n*-pentane dropped approximately 10% in 6 hr of irradiation. Maximum concentrations of products were: formaldehyde, 49 pphm; oxidant, 30 pphm; and peroxyacetyl nitrate (PAN), 6 pphm. The work reported here was undertaken to define more fully the reaction characteristics of the atmosphere by irradiating atmospheric samples in situ.

## Experimental

Atmospheric samples were collected and irradiated in downtown Los Angeles on top of a mobile laboratory truck. Samples were collected in 300-l. plastic (Tedlar) bags between 7:00 and 8:00 A.M., and irradiation began around 8:00 A.M. Half of the irradiations were carried out with two bags irradiated side by side, one exposed to full sunlight and the other enclosed in a screened cage which attenuated the light intensity 58%. New bags required conditioning prior to irradiation to minimize wall effects in the reaction. Conditioning was achieved by irradiating an air sample in the bag for a full day prior to an experiment.

Analyses for total hydrocarbons were obtained with a hydrocarbon flame ionization analyzer (FIA) calibrated with a propane-air mixture. The alkylbenzenes were analyzed on an open tubular column of *m*-bis-*m*-phenoxyphenoxy benzene (300 ft long, 0.06-in. i.d.); the column was maintained at 70°C, and sample volume was 150 cc.

The C<sub>4</sub> to C<sub>7</sub> aliphatics were analyzed on an open tubular dibutylmaleate column (300 ft long, 0.06-in. i.d.) immersed in ice water. A 1 ft long foretrap of 10% Carbowax 1540 on Gas Chrom Z cooled in liquid N<sub>2</sub> was used to concentrate a 90-cc sample. A trap consisting of 1,2,3-tris(2-cyano)ethoxypropane (TCEP) at room temperature was used after the column to prevent bleeding of the substrate to the detector. Samples usually were run every 60 min; however, when hydrocarbon concentrations were unusually high, clearing the column required 90 min.

The C<sub>2</sub> to C<sub>5</sub> aliphatics were analyzed with a silica gel column (grade 58, 8 ft long, 1/8-in. i.d.), acid-washed with HNO<sub>3</sub>. A 72-cc sample was concentrated on a Carbowax trap immersed in liquid N<sub>2</sub> and then was flushed onto the column for 1½ min. The trap was then switched from the column, and the H<sub>2</sub>O and heavier hydrocarbons were flushed out for 1 hr before the next sample was collected.

Analysis for PAN was carried out with a glass column packed with 10% polyethylene glycol 600 on Gas Chrom Z (8 ft long, 1/8-in. i.d.) and a Ni<sup>63</sup> electron capture detector. With a 5-cc sample loop, the system's sensitivity to PAN was 0.1 ppb. The PAN calibration was obtained with calibration mixtures that had been analyzed by ir spectrophotometry using absorptivities reported by Stephens (1964).

Griess-Saltzman reagent was used for determination of NO<sub>2</sub> and NO + NO<sub>2</sub> (NO<sub>x</sub>). Chromium trioxide paper was used to oxidize NO to NO<sub>2</sub>, and the NO analyses were corrected for conversion efficiency of the paper, Neutral KI reagent was used for the oxidant analyses, which were corrected for contributions from NO<sub>2</sub> and PAN.

Light intensity was measured continuously with an Eppley Ultraviolet Sensor (3000–3800Å).

## Results and Discussion

In an earlier study, Altshuller et al. (1970) found that hydrocarbons could be stored without loss in plastic bags for up to 6 hr. Hydrocarbons in the air samples collected in the study

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Table I. Average Initial Composition of the Irradiated Atmospheric Samples

Paraffins	ppbC	Olefins	ppbC	Aromatics	ppbC
Ethane	191	Ethylene	151	Toluene	271
Propane	140	Propylene	60	Ethylbenzene	67
Isobutane	65	1-Butene	47	<i>p</i> -Xylene	100
<i>n</i> -Butane	286	Isobutene		<i>m</i> -Xylene	215
Isopentane	312	<i>trans</i> -2-Butene	12	<i>o</i> -Xylene	87
<i>n</i> -Pentane	171	Methylacetylene		<i>n</i> -Propylbenzene	21
Cyclopentane	138	<i>cis</i> -2-Butene	8	<i>m</i> -Ethyltoluene	111
2-Methylpentane		1,3-Butadiene	11	<i>p</i> -Ethyltoluene	
3-Methylpentane	68	1-Pentene	11	<i>tert</i> -Butylbenzene	23
<i>n</i> -Hexane	82	2-Methyl-1-butene	15	<i>o</i> -Ethyltoluene	
2,4-Dimethylpentane	89	<i>trans</i> -2-Pentene	22	<i>sec</i> -Butylbenzene	137
Cyclohexane	16	<i>cis</i> -2-Pentene	10	1,2,4-Trimethylbenzene	
3-Methylhexane	68	2-Methyl-2-butene	29	1,3,5-Trimethylbenzene	29
<i>n</i> -Heptane	40	1-Hexene	15	Isopropylbenzene	76
Methylcyclohexane	49	Unknown 7	6	Styrene	
Unknown 1	6	Unknown 8	3	Total	1,137
Unknown 2	11	Total	400		
Unknown 3	37			Other	
Unknown 4	28			Nonmethane FIA, ppmC	4.0
Unknown 5	23			CO, ppm	10.3
Unknown 6	80			NO + NO <sub>2</sub> , pphm	41
(Acetylene)	160			Methane, ppm	3.3
Total	2,060				

showed equally good stability in storage; however, there was a 12% loss of NO<sub>2</sub> in 7 hr.

The atmospheric samples irradiated in this study were composed chiefly of paraffins and aromatics, with olefins constituting approximately 11% of the total nonmethane carbon (Table I). Ethylene is the predominant olefin, constituting approximately 38% of the olefins. The samples of this study were also characterized by a strong correlation between total hydrocarbon concentration (FIA) and CO concentration ( $r = 0.94$ ).

The composition of these atmospheric samples is in agreement with that of air samples obtained in a tunnel in Los Angeles (Table II). The agreement with auto exhaust composition is satisfactory except for the paraffin content. The  $\Sigma$  olefin-CO ratio is 15% lower than that found in auto exhaust, but the  $\Sigma$  paraffins (less methane)-CO ratio is twice as great. The  $\Sigma$  C<sub>5</sub><sup>+</sup> paraffins (+ cyclopentane)-CO ratios, however, are in much closer agreement. The higher proportions of C<sub>5</sub> and lighter paraffins in the atmospheric and tunnel samples can be attributed to natural gas and gasoline evaporative losses (Neligan, 1962; Stephens and Burleson, 1967).

From the  $\Sigma$  paraffins (less methane)-CO ratio found in auto exhaust and the average CO concentration in the atmospheric samples one finds that approximately one third of the hydrocarbon concentration (as C) of these atmospheric samples may arise from natural gas and gasoline vapors.

Reaction curves (Figures 1, *a* and *b*) for the irradiated samples are similar to those reported for synthetic laboratory mixtures of hydrocarbons + NO<sub>2</sub> in air. There are also similarities with the reaction curves measured in the open atmosphere, although these are not as close as in the case of the laboratory studies. The early part of the reaction is characterized by the conversion of nitric oxide to NO<sub>2</sub>. Some loss of NO<sub>2</sub> during this conversion is indicated by the NO<sub>2</sub> peak concentration, which is lower than the initial NO<sub>2</sub> concentration.

After the NO<sub>2</sub> peak is reached, the NO<sub>2</sub> concentration drops off rapidly as both PAN and oxidant are formed. Reduction of light intensity shifts the reaction curve to the right, and may or may not decrease product yields.

Results obtained in the irradiation of the atmospheric samples are presented in Table III. The initial hydrocarbon concentrations ( $\Sigma$ HC<sub>0</sub>) are the sums of the concentrations of nonmethane hydrocarbons analyzed by gas chromatography. On the average, these sums constituted 90% of the average FIA nonmethane hydrocarbon concentration. Maximum values obtained for various measures of reactivity were: maximum oxidant concentration, 39 pphm; maximum PAN concentration, 9.7 pphm; 4-hr oxidant dosage, 118 pphm/hr; 4-hr PAN dosage, 38 pphm/hr; 4-hr NO<sub>2</sub> dosage, 239 pphm/hr; loss of olefins plus alkylbenzenes in 4 hr, 49%.

The irradiation of 10/23 was an impromptu experiment which was carried out because the level of pollution in the morning of that day was extremely high. The relatively low oxidant yield obtained is attributed to omission of the routine bag conditioning procedure prior to irradiation. Generally, atmospheric samples producing highest oxidant concentrations, highest losses of olefins plus aromatics, and highest NO<sub>2</sub> formation rates were associated with both high hydrocarbon and high NO<sub>x</sub> concentrations. Three different samples produced 38-39 pphm oxidant. This oxidant concentration was produced over a range of reaction conditions (Table IV). The initial hydrocarbon concentrations are the only conditions which are closely comparable in the three samples. These hydrocarbon concentrations, producing highest oxidant, are also among highest concentrations which occurred in the study.

Relative rates of hydrocarbon consumption, based on percent loss per hour, are shown in Table V. The rates of ethane, propane, isobutane, and acetylene in our study are not significantly different from zero. However, significant loss of

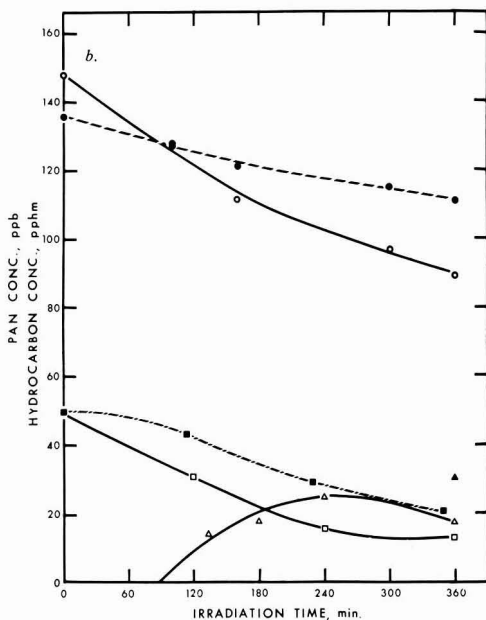
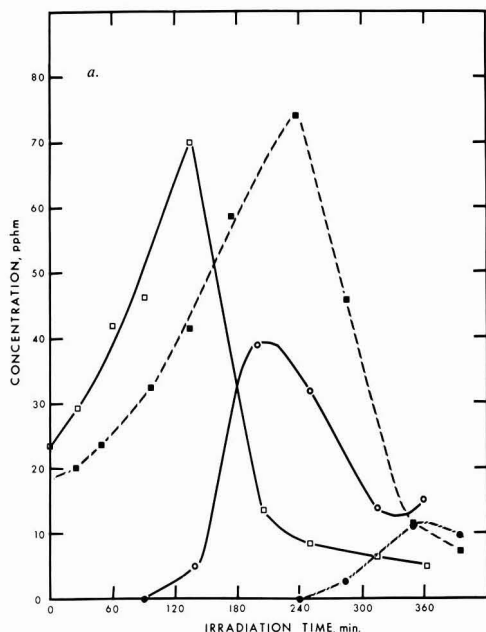


Figure 1. Reaction curve for irradiated atmospheric sample of Oct. 17, 1968

- a.   
 □—□ NO<sub>2</sub>, full sunlight intensity   
 ■---■ NO<sub>2</sub>, attenuated intensity   
 ○—○ Oxidant, full sunlight intensity   
 ●---● Oxidant, attenuated intensity
- b.   
 ○—○ Aromatics, full sunlight intensity   
 ●---● Aromatics, attenuated intensity   
 □—□ Olefins, full sunlight intensity   
 ■---■ Olefins, attenuated intensity   
 △—△ PAN, full sunlight intensity   
 ▲---▲ PAN, attenuated intensity

Table II. Comparison of the Composition of Atmospheric Samples with Tunnel Samples and Auto Exhaust Samples

	Auto exhaust (base line cars)	Los Angeles, 2nd St. tunnel samples	Los Angeles atm samples (this study)
Ratio × 100			
Ethylene			
Σ olefins	31.5	44.5	37.8
Ethylene			
CO	1.5	1.7	1.5
Acetylene			
CO	1.37	1.67	1.55
Σ olefins			
CO	4.6	3.9	3.9
Σ aromatics			
CO	14.3	14.0	13.4
Σ paraffins (less methane)			
CO	7.9	14.4	18.8
Σ C <sub>5</sub> <sup>+</sup> paraffins + cyclopentane			
CO	5.8	7.2	7.1

<sup>a</sup> Bonamassa and Wong-Woo, 1966.

<sup>b</sup> EPA Air Pollution Control Office and California Air Resources Board (1970).

the heavier paraffins confirms observations reported in an earlier study (Altshuller et al., 1968, 1970). 2-4-Dimethylpentane was found to be as reactive as ethylene and more reactive than toluene.

The relative reactivities of the hydrocarbons in this study are in substantial agreement with those reported by others (Stephens and Burleson, 1967; Heuss and Glasson, 1968; Leach et al., 1964). The results of Leach et al. were obtained with irradiated samples of auto exhaust. In that study the relative reaction rates of many hydrocarbons increased as the HC-NO<sub>x</sub> ratio was decreased from 12-1 to 3-1. For these hydrocarbons the range of rates is presented in Table V. The results of Heuss and Glasson were obtained from individual mixtures of each hydrocarbon and nitric oxide in air. The only serious differences between results of this study and those of Heuss and Glasson are the relative rates for 2-methyl-2-butene and *sec*-butylbenzene. The calculated rates for 2-methyl-2-butene are probably in error in both studies because they were obtained from measurements made some time after virtually all of the compound had reacted. The study of Stephens and Burleson was made with atmospheric samples collected in glass vessels and irradiated with Blacklite fluorescent lights.

Thus, the present results substantiate the effectiveness of irradiation chamber experiments in simulating the rates of reaction of hydrocarbons in actual atmospheric mixtures subjected to solar irradiation with proviso that in drawing inferences from laboratory measurements as to the behavior of the real atmosphere, the more dynamic nature of the open atmosphere must always be kept in mind.

All paraffins except isobutane and those of lower molecular weight were found to react in the atmospheric samples. Table VI presents percentage loss of individual hydrocarbons for one sample which exhibited relatively high reactivity. The loss of paraffins generally increases with molecular weight, some C<sub>7</sub> paraffins exhibiting half-lives as short as 6 hr of daylight. This result is in marked contrast to the study of Stephens

Table III. Irradiation of Atmospheric Samples Collected in Downtown Los Angeles, September–November 1968

Date	$\Sigma\text{HC}_n$ , ppbC	$(\text{NO}_x)_n$ , pphm	4-hr uv dosage, MW/hr/cm <sup>-2</sup>	Olefins + aromatics reacted, ppbC	Max. oxidant formed, pphm	Max. PAN formed, ppb
11/13	2,224	28	10.1	387	23	66
11/12	1,317	13	4.8	172	5	27
11/7	4,367	60	6.4	811	39	97
10/31	2,028	23	4.9	256	2	16
10/24	5,193	95	7.7	922	38	40
10/23	9,990	106	7.5	1599	28	54
10/17	4,529	87	8.5	915	39	25
10/10	2,693	49	1.9	127	10	9
10/4 <sup>a</sup>	1,509	18	1.4	91	1	8
9/12	(2,037)	22	10.2	...	14	21
9/11	(4,293)	17	10.2	...	20	45
9/10	2,503	22	9.1	141	4	10
9/6	4,548	20	9.7	406	9	38
9/5	2,534	9	10.2	314	3	16

and Scott (1962) in which no loss of saturates was observed, but is in general agreement with the results of Stephens et al. (1967). This reactivity of paraffins serves as one criterion of adequate simulation of atmospheric reactions in laboratory irradiation chambers. Those laboratories which do not perceive any significant reaction of paraffins may be operating at unrealistically low light intensities. The C<sub>3</sub> and lighter paraffins, which characterize natural gas and gasoline evaporative emissions in the Los Angeles Basin, accounted for 19% of the total hydrocarbon loss (measured as C) after 6 hr of irradiation.

There is considerable overlap in percentage losses of the paraffins and aromatics. Of the aromatic components analyzed only the 1,3,5-trimethylbenzene and the *sec*-butylbenzene plus 1,2,4-trimethylbenzene are distinctly more reactive than 2,4-dimethylpentane. The only explanation which can be offered for the lack of reactivity of isopropylbenzene and *n*-propylbenzene is that the gas chromatograph peaks may be mostly some other, nonreactive compounds. The earlier irradiation study of Altshuller et al. (1968) also showed no discernible loss of these compounds. However, both the studies of Kopczyński (1964) and Heuss and Glass (1968) showed these compounds to be at least as reactive as ethylbenzene. Although isopropylbenzene could not be separated from styrene in this analysis, it is apparent that no measurable concentration of styrene is present in this sample. The olefins as a class are seen to be the most reactive compounds. All the olefins except ethylene, propylene, and 1-butene had half-lives of 2 hr or less. *Cis*-2-pentene and 2-methyl-2-butene were completely reacted in 2 hr.

Table IV. Conditions Under Which 38–39 Pphm Oxidant Was Formed

	Nov. 7	Oct. 24	Oct. 17
Temp, °F	64–76	80–98	75–87
4-hr dosage of uv light, MW/hr/cm <sup>-2</sup>	6.4	7.7	8.5
Hydrocarbon/NO <sub>x</sub> ratio	7.3	5.5	5.2
Initial HC concn, ppbC	4,367	5,193	4,529
Initial NO <sub>x</sub> concn, pphm	60	95	87

Table VII shows correlation coefficients computed for various reaction parameters and reactivity measures. Correlation coefficients of 0.66 and 0.46 represent significance at the 1% and 10% alpha risk levels, respectively, except in the case of maximum NO<sub>2</sub> formation rate. In this case only seven samples could be used for measurement. Consequently, where this measure is concerned, correlation coefficients of 0.80 and 0.58 represent significance at the 1% and 10% alpha risk levels, respectively.

The various reactivity measures generally correlated well with each other, except in the case of maximum NO<sub>2</sub> formation rate. The reactivity measure which showed best overall correlations with initial reactant concentrations and other reactivity measures was the quantity of olefins plus aromatics reacted. Only the amount of olefins plus aromatics reacted was strongly correlated with the maximum NO<sub>2</sub> formation rate. The quantity of olefins plus aromatics reacted, maximum oxidant, and maximum NO<sub>2</sub> formation rate correlated well with the initial hydrocarbon concentration, and with the initial NO<sub>x</sub> concentration. The amount of olefins plus aromatics reacted correlated best with initial hydrocarbon concentration and with initial NO<sub>x</sub> concentration. None of the reactivity measures were significantly correlated with either the hydrocarbon-NO<sub>x</sub> ratio although the ratio ranged from 5/1 to 28/1 or the 4-hr uv dosage.

However, before conclusions are drawn about the effect of the hydrocarbon-NO<sub>x</sub> ratio, it would be advisable to study irradiated air samples with the other reaction variables held constant. Correlation between the uv radiation dosage and percent loss of olefins was high ( $r = 0.81$ ). The coefficients obtained for aromatics and paraffins were only 0.44 and 0.54, respectively. The percent loss of olefins showed a negative correlation coefficient of 0.48 with hydrocarbon-NO<sub>x</sub> ratio, which is significant at the 10% risk level.

The effect of ultraviolet radiation dosage, which in the correlation analyses was largely obscured by other variables, was studied by comparing bag samples irradiated simultaneously at two different intensities. A reduction of light intensity shifts the reaction curve to the right, but effects of a 58% reduction in light intensity on product yields varied over a considerable range. The reduction in peak oxidant and oxidant dosage ranged from 100% to 60%. Peak PAN con-

**Table V. Relative Rates of Percentage Loss of Selected Hydrocarbons Averaged Over 4-Hr Irradiation**

Hydrocarbon	Rel rate	Std dev	Stephens and Burleson (4-hr irradsn)	Heuss and Glasson (6-hr irradsn)	Leach et al. (auto exhaust)
Ethane	0.06	0.09			
Propane	0.16	0.09	0.18		
<i>n</i> -Butane	0.27	0.13	0.37	0.11	0.3
Isobutane	0.24	0.26	0.33		
<i>n</i> -Pentane	0.37	0.07			
Isopentane	0.43	0.13	0.58		
2,4-Dimethylpentane	0.99	0.27			
Acetylene	0.14	0.07	0.17		
Ethylene	1.00		1.0	1.00	1.00
Propylene	2.33	0.42	2.5	1.6	1.95-2.50
1-Butene	1.62 <sup>a</sup>	0.52	2.5	1.9	
2-Methyl-2-butene	9.39 <sup>b</sup>	1.99		2.1	
Toluene	0.56	0.34		0.87	0.59
<i>m</i> -Xylene	1.14	0.45		1.2	1.13-1.59
<i>o</i> -Xylene	0.70	0.28		1.2	0.74-1.27
<i>sec</i> -Butylbenzene	1.25 <sup>c</sup>	0.45		0.47	

<sup>a</sup> Contains isobutylene.

<sup>b</sup> Averaged over first hour of irradiation.

<sup>c</sup> Contains 1,2,4-trimethylbenzene.

**Table VI. Loss of Hydrocarbons After 6-Hr Irradiation, 10/17/68**

Paraffins	%	Olefins	%	Aromatics	%
Ethane	2	Ethylene	57	Toluene	34
Propane	0	Propylene	84	Ethylbenzene	19
Isobutane	6	1-Butene	64	<i>p</i> -Xylene	29
<i>n</i> -Butane	14	Isobutene		<i>m</i> -Xylene	51
		<i>trans</i> -2-Butene } Methylacetylene }	55		
Isopentane	24	<i>cis</i> -2-Butene	67	<i>o</i> -Xylene	33
<i>n</i> -Pentane	26	1,3-Butadiene	100	Isopropylbenzene } Styrene }	0
Cyclopentane } 2-Methylpentane }	35	1-Pentene	92	<i>n</i> -Propylbenzene	0
		2-Methyl-1-butene	100	<i>m</i> -Ethyltoluene } <i>p</i> -Ethyltoluene }	49
<i>n</i> -Hexane	29	<i>trans</i> -2-Pentene } 2,2-Dimethylbutane }	70	<i>tert</i> -Butylbenzene } <i>o</i> -Ethyltoluene }	46
2,4-Dimethylpentane	48	<i>cis</i> -2-Pentene	100	<i>sec</i> -Butylbenzene } 1,2,4-Trimethylbenzene }	63
Cyclohexane	39	2-Methyl-2-butene	100	1,3,5-Trimethylbenzene	78
3-Methylhexane	38	1-Hexene	100		
<i>n</i> -Heptane	43				
Methylcyclohexane	45				
(Acetylene)	4				

**Table VII. Correlation Coefficients**

	Max. oxidant	Oxidant dosage	Max. PAN	PAN dosage	Olefins + aromatics reacted	Max. NO <sub>2</sub> formation rate
ΣHC <sub>0</sub>	0.60	0.62	0.33	0.54	0.95	0.95
(NO <sub>2</sub> ) <sub>0</sub>	0.76	0.69	0.28	0.32	0.88	0.90
ΣHC <sub>0</sub> /(NO <sub>2</sub> ) <sub>0</sub>	-0.31	-0.25	-0.13	0.07	-0.18	-0.16
4-Hr uv dosage	0.34	0.42	0.28	0.39	0.35	0.35
Max. oxidant		0.95	0.71	0.66	0.78	0.61
Oxidant dosage			0.76	0.74	0.81	0.69
Max. PAN				0.97	0.54	0.35
PAN dosage					0.62	0.49
Olefins + aromatics reacted						0.94



**Table VIII. Effect of Uv Radiation Intensity on Reactivity Measures**

Date	Time to NO <sub>2</sub> peak			Time to half the oxidant peak		
	Time, min		Ratio, attenuated/full	Time, min		Ratio attenuated/full
	Attenuated intensity	Full intensity		Attenuated intensity	Full intensity	
11/7	226	78	2.9	315	146	2.2
10/24	186	99	1.9	275	115	2.4
10/23	165	75	2.2	245	93	2.6
10/17	237	135	1.8	315	169	1.9
9/26	215	136	1.6	294	160	1.8
Av			2.1			2.2

centration was less consistent, ranging from 100% decrease to a 28% increase. PAN dosage ranged from a 90% decrease to no decrease at all. NO<sub>2</sub> dosage averaged a 25% increase, with one sample, taken on a day of very low uv intensity, showing a 16% decrease. However, decreased uv radiation intensity did produce a rather consistent effect on two measures of reactivity: time to NO<sub>2</sub> peak and time to half the oxidant peak (Table VIII). In both cases, the 58% reduction in uv intensity increased these times by a factor 2.1 to 1 and 2.2 to 1, respectively. These factors are approximately the inverse ratio of the light intensities in the two bags 0.42, and it is evident that the two bags required equal uv radiation dosage to reach the NO<sub>2</sub> peak and also half the oxidant peak.

The effect of a 58% reduction in light intensity on the percent of hydrocarbons lost was least for the olefins, the most reactive class of hydrocarbons, and greatest for the paraffins, the least reactive class (Table IX). The lesser reduction in observed olefin losses can be attributed in part to the fact that some of the olefins were completely reacted in less than 4 hr. At full light intensity, the 4-hr uv light dosage averaged

7.5 MW/hr/cm<sup>2</sup>, and the amount of paraffins reacted constitutes 28% of the reacted C atoms. On days of greater light intensity, and over a full day of irradiation, one can expect even greater participation of the paraffins in the photochemical reactions of the atmosphere.

As a class (excluding methane), the paraffins showed one fifth the average reactivity (percentage consumption) of the olefins, and the aromatics, one half. The aromatics, however, accounted for the greatest yield of reacted carbon atoms in the atmospheric samples irradiated for 4 hr at full sunlight intensity.

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**Table IX. Average Hydrocarbon Losses in Samples Irradiated at Full Intensity and at 42% Full Intensity**

	Initial concn, ppbC	Amount reacted in 4 hr, ppbC	Loss, %	Ratio of losses, attenuated/full
Paraffins				
Full	2,385	252	11	0.29
Attenuated	2,337	72	3	
Olefins				
Full	485	267	55	0.65
Attenuated	481	174	36	
Aromatics				
Full	1,275	368	29	0.41
Attenuated	1,190	151	13	

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# Critical Evaluation of Saltzman Technique for NO<sub>x</sub> Analysis in the 0–100 Ppm Range

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■ The Saltzman technique for batch NO<sub>x</sub> analysis from flames, about 95% of which is NO, has been critically evaluated using pure oxygen as the oxidizer. Optimum operating conditions are established as dilution of the flame sample with pure oxygen to 50% partial pressure, and a residence time in the absorbing flask of about 24 hr. The ASTM standard phenol disulfonic acid procedure for NO<sub>2</sub> analysis is shown to give values which are too low if the oxygen content is greater than 20%.

A reliable and interference-free technique for NO<sub>x</sub> analyses in the range 0–100 ppm is required for studying flames in the laboratory. The two currently accepted analytical methods, the Saltzman technique (1966) and the phenyl disulfonic acid procedure (1967) (PDA) have not previously been adequately evaluated as to interference from oxygen, surface-to-volume ratio, etc. For precise work, recent authors (Fenimore, 1970; Harris et al., 1970) rely on the ASTM standard PDA procedure (the results of which are shown here to be too low when excess oxygen is present). The method is so tedious and time-consuming that, for detailed systematic investigations of flames, recourse must be made to the less accurate, but far less tedious, Saltzman procedure.

The purpose of this investigation is to evaluate critically the Saltzman procedure and to make the necessary modifications so that accurate and reliable results may be obtained.

## Theoretical Approach

The kinetics of the oxidation of nitric oxide to nitrogen dioxide have frequently been studied and are well-understood (Baulch et al., 1970). The oxidation occurs via a homogeneous three-body reaction:



The rate of production of NO<sub>2</sub> is given by

$$\frac{d(\text{NO}_2)}{dt} = k(\text{NO})^2(\text{O}_2) \quad (2)$$

where the rate constant  $k = 2.4 \times 10^9 \exp(1046/RT) \text{ cm}^6 \text{ mol}^{-2} \text{ sec}^{-1}$ . Integrating [by assuming (O<sub>2</sub>) to be constant] and converting to the appropriate units, the concentration of NO<sub>2</sub> (in ppm) present at any time,  $t$ , is given by

$$(\text{NO}_2) = \frac{2.28 \times 10^{-7} t (\text{NO})_{\text{init}}^2 (\% \text{O}_2)}{2.28 \times 10^{-7} t (\% \text{O}_2) (\text{NO})_{\text{init}} + 1} \quad (3)$$

where (NO)<sub>init</sub> is the initial NO concentration in ppm, (% O<sub>2</sub>) is the initial O<sub>2</sub> concentration in %, and  $t$  is the time in sec. Equation 3 is depicted graphically in Figure 1 as a plot of (NO<sub>2</sub>) vs.  $t$  (in hr). In drawing the curves, it was assumed

that the flame gas sample originally contained 0% oxygen, the required amount of oxygen being added as a diluent. The (NO)<sub>init</sub> of Equation 3 is corrected to take account of the dilution step. The curves are sigmoid-shaped. After 24 hr have elapsed, the curve for the 1% oxygen sample is seen to be still increasing, whereas 96% conversion had occurred in the samples containing 50% and 60% O<sub>2</sub>. Figure 2A is a plot of (NO<sub>2</sub>)/(NO)<sub>init</sub> vs. % O<sub>2</sub> at 24 hr reaction time, for various initial amounts of NO, the curves again being derived from Equation 2 by assuming that the oxygen was added as a diluent. The curves peak at about 50% O<sub>2</sub> for all NO concentrations, the peak being more marked at NO concentrations below 10 ppm. If the oxygen were present in the original flame sample and no oxygen were added as a diluent, then the curves in Figure 2A would not have a maximum. It is important to note that Equations 2 and 3 in themselves do not predict a peak; the peak arises from the oxygen diluting the system, causing the effective NO concentration to decrease.

Figure 3 is a plot of percentage conversion of NO to NO<sub>2</sub> (at 24 hr reaction time) vs. NO concentration in the flame, for a sample which has the optimum amount of oxygen added as a diluent, namely 50%. Figure 4, based on Figure 3, is a plot of the actual error in the NO concentration vs. the NO concentration in the flame. Although the sharp fall-off of Figure 3 is alarming, Figure 4 shows that above 25 ppm NO, the Saltzman procedure as modified here for NO<sub>2</sub> (24 hr reaction time and 50% O<sub>2</sub> present) gives rise to a constant error of 2 ppm. If the measured value falls below 25 ppm NO, the correction which should be added to the measured value may be read directly from Figure 4.

## Experimental

All the gas samples for analysis were taken from a premixed Cambridge City gas-air burner, gas flow rates being metered on flowmeters. Gas chromatographic analyses of the pre-

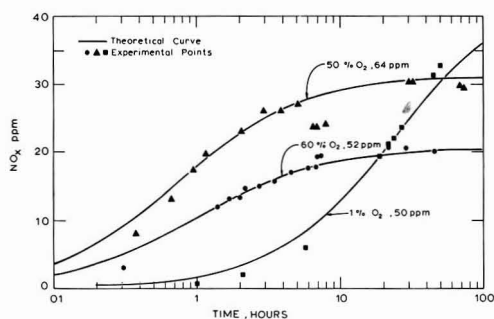


Figure 1. Rate of conversion of NO to NO<sub>2</sub> at different O<sub>2</sub> concentrations

Solid lines are theoretical predictions; points are experimental data

mixed unlit gas mixture were carried out before each series of experiments to check the accuracy of the gas flow settings. A reproducibility of better than  $\pm 0.5\%$  was obtained in this manner.

An 18-in. long (0.030-in. i.d.) stainless steel water-cooled sample probe was used to withdraw gas samples 1 in. from the burner surface. Apart from  $\text{NO}_x$ , the gas sample contained 86.19%  $\text{N}_2$ , 0.00%  $\text{O}_2$ , 8.58%  $\text{CO}_2$ , and 5.59%  $\text{CO}$  (on a dry basis). A drying agent such as silica gel or Drierite was found to reduce substantially the measured  $\text{NO}_x$  concentrations, and no drying agent was used during  $\text{NO}_x$  analyses. To reduce  $\text{NO}_x$  losses within the interconnecting tubing, the distance from the probe to the absorption flasks was kept as short as possible (about 8 in.).

For the Saltzman and PDA procedures, the specified reagents were used. Oxygen was taken from a standard gas cylinder. Nitric oxide of 98.5% purity (Air Products) was purified before use by repeated low-temperature vacuum distillation.

The kinetic studies of the Saltzman procedure were carried out using a 1-liter borosilicate glass flask on which a standard 1-cm width quartz uv colorimeter cell was attached. It was possible with this apparatus to monitor the progress of the Saltzman reaction on the colorimeter without in any way disturbing the solution in the flask. It was therefore possible to ascertain what values the Saltzman method would have given, had the reaction been stopped at that stage.

The absorption flasks were thoroughly cleaned with chromic acid prior to use. Each flask, containing 25 ml of Saltzman reagent, was evacuated to a pressure corresponding to the boiling point of the solution (about 15 mm Hg) and the gas sample slowly drawn in. If oxygen was to be added, the flask was not filled up to atmospheric pressure, but to some lower pressure corresponding to the partial pressure of sample required. Pure oxygen was then added to the flask until the total pressure (sample plus oxygen) equaled 1 atm.

Steady-flow mixtures containing a known amount (in the range 1–100 ppm) of nitric oxide in nitrogen for calibration purposes were prepared by positive displacement of nitric oxide with a constant head of mercury from a glass storage vessel into a much larger stream of nitrogen. The nitrogen flow rate, approximately 40,000 times that of the nitric oxide, was monitored on a wet test meter. The flow rate of nitric oxide (99.9% pure) was measured to within  $\pm 0.2\%$ , that of the nitrogen (99.995% pure) to within  $\pm 0.2\%$ . The system was allowed to equilibrate for at least 2 hr before calibration. The calibration procedure utilized the identical sample probe and interconnecting tubing as used for flame probing.

### Experimental Results and Discussion

Results of the kinetic experiments described above are shown in Figure 1 as a plot of  $(\text{NO}_x)$  vs. time. For example, in a sample containing 52 ppm of  $\text{NO}_x$ , and subsequently diluted with 50% oxygen, the conversion is 95% complete within 24 hr. The experimental data points fall close to the theoretical curves as predicted from the integrated rate expression, confirming the obvious that the key step is indeed the oxidation of  $\text{NO}$  to  $\text{NO}_2$ .

Figure 2B is a plot of the measured  $\text{NO}_2$  concentration, for both the Saltzman and PDA methods, vs. the oxygen partial pressure (as a percentage of the total) for varying amounts of oxygen added as a diluent. The reaction time was kept constant at 24 hr. For the Saltzman procedure, the measured  $\text{NO}_2$  concentration (corrected for dilution with oxygen) is seen to increase as oxygen is added, reaching an asymptote at approximately 50% excess oxygen, in agreement with the

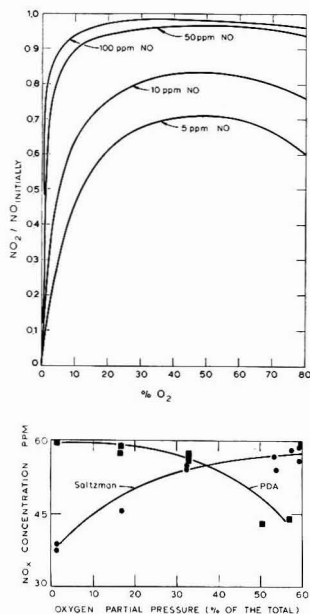


Figure 2. Effect of oxygen concentrations on the conversion of  $\text{NO}$  to  $\text{NO}_2$  at 24 hr reaction time

- A. Using Equation 2
- B. Experimental results of both Saltzman and PDA procedures

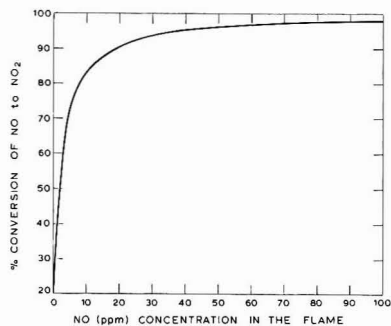


Figure 3. Percentage conversion of  $\text{NO}$  to  $\text{NO}_2$  for various initial  $\text{NO}$  concentrations (24 hr reaction time and 50%  $\text{O}_2$  concentration)

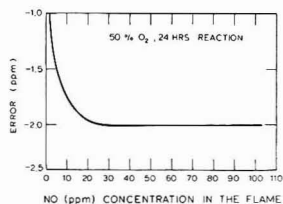


Figure 4. Absolute error in ppm  $\text{NO}$  vs.  $\text{NO}$  concentration in the flame (24 hr reaction time and 50%  $\text{O}_2$  concentration)

predictions of Figure 2A. For the PDA procedure, the measured NO<sub>x</sub> concentration (corrected for dilution with oxygen) decreases with increasing oxygen content! This is not entirely unexpected, as the Saltzman reagent is known to absorb NO<sub>2</sub> in about 10 min as compared to the PDA reagents' 24 hr. Thus, at the higher O<sub>2</sub> levels, where the oxidation to NO<sub>2</sub> is more rapid, it is conceivable that not all of the NO<sub>2</sub> is absorbed into the PDA solution before a significant fraction is adsorbed onto the glass walls. Greig and Hall (1966) have shown that at concentrations of the order of 50 ppm, adsorption of NO<sub>2</sub> on solid surfaces is significant. The two curves of Figure 2B stress the importance of testing the analytical method for background interference from the very parameters which are to be varied. Meaningless results would have been obtained if either the Saltzman or PDA analytical methods had been used without modification for investigating the effects of excess oxygen on NO<sub>x</sub> production (Williams et al., 1971).

The reproducibility of the method was tested by analyzing five identical samples taken on five successive days. After correcting for the small differences in the flask volume and the pressure, the results were identical. The reproducibility of the method is established to better than  $\pm 0.3\%$ .

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## Properties of Carbonate Rocks Related to SO<sub>2</sub> Reactivity

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■ Petrographic examination and grain size-distribution measurements were made on 11 specimens representing a broad spectrum of limestones and dolomites. The SO<sub>2</sub> reaction kinetics of calcines prepared from each rock type were determined at 980°C. Stones of various geological types yield calcines of distinctly different physical structures that show correspondingly large differences in both rate of reaction and capacity for SO<sub>2</sub> sorption. Pore size and particle size together determine the extent to which the interiors of individual particles react. Particles smaller than 0.01 cm with pores larger than 0.1  $\mu$  react throughout their internal pore structure at a rate directly proportional to the BET surface. The rate decays exponentially as sulfation proceeds until the pores are filled with reaction product. The ultimate capacity of small particles is determined by the pore volume available for product accumulation, which is generally equivalent to about 50% conversion of the CaO in limestones. Variations in effectiveness of carbonate rocks for flue gas desulfurization are explained by the physical properties of their calcines, which are related to the crystal structure of the original rock. The high reaction rates achieved in the limestone injection process apparently result from the large surface area existing for short periods immediately following the dissociation of CaCO<sub>3</sub>.

The wide variation in SO<sub>2</sub> reactivity of different naturally occurring rocks that was noted in early laboratory studies (Harrington et al., 1968) has proved to be a major factor in the development of limestone-based processes for SO<sub>2</sub> control. The degree of flue gas desulfurization achieved in pilot plant evaluation of the limestone injection process (Attig and Sedor, 1970) ranged from less than 5% to 43% when 100 stones were tested at an injection rate stoichiometrically equivalent to SO<sub>2</sub>. Different stones tested in the fluidized-bed combustion process also gave various results (Davidson and Small, 1970). An understanding of the cause of these variations is needed if the most suitable selection is to be made from available limestone sources and maximum desulfurization obtained by either process.

Laboratory tests of a large number of carbonate rocks showed no relationship between chemical composition and SO<sub>2</sub> reactivity (Harrington et al., 1968; Potter, 1969). Good correlation of SO<sub>2</sub> saturation capacity with the pore volume of calcines ( $\bar{D}_p = 0.092$  cm) has been found (Falkenberg and Slack, 1969; Potter, 1969), suggesting the primary importance of physical properties. Kinetic studies (Borgwardt, 1970a) demonstrated the participation of the internal pore structure in the reaction with SO<sub>2</sub> and showed that the rate of reaction also differs considerably among stones, even when chemical

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reaction is controlling. That kinetic study is extended here to include an analysis of the effect of pore structure on the reactivity of calcined stones and to compare the pore structures developed by rocks of different geological type.

#### Materials and Methods

Eleven diverse types of carbonate rock were characterized petrographically by a polarizing microscope and a scanning electron microscope (SEM). Pore and grain characteristics were compared on polished and fractured surfaces with the SEM. Pore volume was determined by weight measurements of water-saturated and water-immersed specimens. Grain sizes were measured with the polarizing microscope, counting about 500 grains in one to four thin sections of each sample. Analyses of the observed distributions were made according to the method presented by Rose (1968) with minor modifications. Mineralogical analyses were made by X-ray diffraction.

Each type of rock was prepared for SO<sub>2</sub> reactivity measurements by calcining it in an Inconel kiln, 8-cm diam by 12.5 cm long, which was rotated at 1 rpm in an electric furnace. Batches (180 grams) of 10/28-mesh rock were calcined at 980°C for 2 hr, except where otherwise noted. The calcine was crushed and screened into three particle size ranges: 12/16 (Tyler) mesh,  $\bar{D}_p = 0.13$  cm; 42/65 mesh,  $\bar{D}_p = 0.025$  cm; and 150/170 mesh,  $\bar{D}_p = 0.0096$  cm. The pore and surface properties of each calcine were determined by standard mercury porosimetry and BET methods. Selected calcine samples were also examined by SEM to observe the pore and grain structure and by chemical analysis to ensure homo-

geneity among the various sized particles. Further, selected samples of SO<sub>2</sub>-reacted calcines were analyzed with an electron microprobe to ascertain the sulfate distribution within individual particles.

Isothermal reaction rates were measured in a differential reactor (Borgwardt, 1970a) exposing 30 mg of calcine to flue gas containing 3000 ppm SO<sub>2</sub>, dry basis ( $2.63 \times 10^{-8}$  g-mol/cm<sup>3</sup>, wet basis, 980°C). The data were correlated by the expression for reaction in porous solids:

$$\frac{1}{W} \frac{dn'}{dt} = \frac{k_p}{\rho_p} C_{SO_2} \eta \quad (1)$$

Because of the uncertainties involved in measuring particle densities,  $\rho_p$ , of finely divided calcines, the rate data are correlated in this study on the basis of CaO surface area,  $S_p$ , which is more accurately and easily determined. Since  $k_p = k_s \rho_p S_p f$ ,

$$r_0 = \frac{1}{Wf} \frac{dn'}{dt} = k_s S_p C_{SO_2} \eta \quad (2)$$

where  $k_s$  is the reaction rate constant per unit CaO surface, cm/sec, and  $f$  is the weight fraction of CaO in the calcine. Values of  $S_p$  were obtained from BET measurements and are expressed in cm<sup>2</sup>/g. Reaction characteristics of the calcines are compared and interpreted according to the initial reaction rate,  $r_0$ , defined by Equation 2.

The effectiveness factor,  $\eta$ , is used here to represent the degree to which reaction occurs within the internal structure of

Table I. Petrographic Description and Mineralogy of Carbonate Rocks

Sample type	Rock or mineral	Distinguishing characteristics	Major component, %	Minor and trace components	Grain shape	Other textural features
1	Calcite	Iceland spar	calcite 100	None detected	Cleavage rhombs	Nearly perfect crystals
2	Calcite	Abundant crystal defects	calcite 100	Traces of soluble Cl and SO <sub>3</sub> salts	Cleavage rhombs	Abundant solid inclusions and twin lamellae; subgrains
3	Limestone	Coarse-grained, high purity	calcite 91	8% dolomite, 1% limonite	Anhedral	Inequigranular; fossil fragments
4	Limestone	Fine-grained, high purity	calcite 98	2% quartz	Anhedral	Equigranular, dense; a few veinlets with medium grains of clear calcite
5	Dolomite	Reef type, high purity	dolomite 99	1% calcite	Anhedral	Recrystallized granular
6	Dolomite	Nonreef type, clayey and silty	dolomite 81	9% quartz, 4% calcite, 5% clay	Anhedral, rhombic	Equigranular, rhombic grains next to pores. Clay along bedding planes; iron oxide along dolomite grains
7	Magnesite	Fine-grained, high purity	magnesite 99	0.5% quartz plus clay	Anhedral, rhombic	Equigranular
8	Aragonite	Oolitic and strontium-bearing	aragonite 96+	About 3% Mg-calcite and 1% clay	Fibrous, bladed	Elliptical and cylindrical remains of marine organisms
9	Dolomite	Limonite- and calcite-bearing	dolomite 70	18% calcite, 5% quartz, 2% clay, 5% limonite	Anhedral, rhombic	Equigranular, rhombic grains along pores; fibrous limonite (?) along dolomite grains
10	Marble	Coarse-grained	calcite 98	2% tremolite, trace of mica	Cleavage rhombs	Abundant intracrystalline inclusions and twin lamellae
11	Marl (Mich.)	Fine, unconsolidated	calcite 84	12% woody organic matter, 3% clay, 1% quartz silt	Rhombic, platy	Porous, agglomerated calcite grains; incoherent

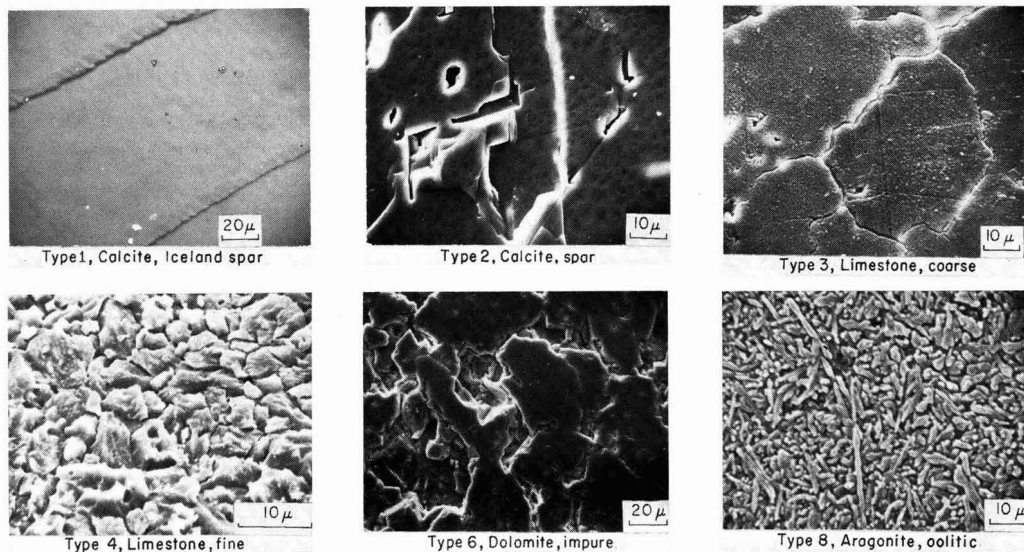


Figure 1. Typical surface textures of carbonate rocks

the solid. The maximum value of  $\eta = 1$  indicates that reaction occurs equally throughout the internal pore structure. Low effectiveness factors,  $\eta \ll 1$ , are associated with strong pore diffusion resistances and indicate that internal structure does not participate in the reaction—i.e., that reaction takes place primarily on the outside surface of individual particles. By analogy with heterogeneous catalytic reactions of first order,  $\eta$  would be expected to be a function of particle size and the ratio, reaction rate/pore diffusion rate. All other factors being equal,  $\eta$  decreases with increasing particle size, increasing temperature or reaction rate, and decreasing pore size.

The effectiveness factor for the noncatalytic system treated here is subject to vary with the degree of solid conversion, therefore all values of  $\eta$  are reported and compared at zero

conversion by extrapolation to initial conditions. This was done by plotting the reaction rates, measured at varying degrees of sulfation, according to the empirical relationship:

$$r = r_0 e^{-\beta n'/W} \quad (3)$$

A plot of  $\log r$  vs.  $n'/W$  yields a straight line of slope  $\beta$  for conversions up to approximately 50% of the CaO in small particles. Extrapolation of the linear region of these plots to  $n'/W = 0$  permitted the initial rate,  $r_0$ , to be evaluated independently of the effects of solid conversion. Plots of the rate data were made for three different particle sizes of each calcine to obtain  $r_0$  and  $\beta$  for each particle size. The initial effectiveness factors were estimated as the ratio of the initial

Table II. Grain Size and Pore Structure of Samples

Sample type number	Grain size					Arithmetic mean, $\mu$	Mean pore volume, cc/g	Pore structure
	Frequency %							
	<8 $\mu$	8–16 $\mu$	16–32 $\mu$	32–63 $\mu$	>63 $\mu$			Character and size of pores
1	0	0	0	0	100	1000	0.000	None obsd
2	0	0	0	0	100	1000	0.004	Intragranular, mainly 0.5–2 $\mu$
3	55.3	24.6	8.8	3.3	8.0	33	0.020	Inter- and intragranular, wide size range
4	95.5	4.2	0.1	0	0.1	4	0.007	Intergranular, mainly 1 $\mu$
5	7.1	2.6	21.3	44.6	24.2	70	0.010	Intergranular, mainly 0.2 mm, and intragranular, mainly 1 $\mu$
6	30.1	30.8	34.3	2.7	2.1	17	0.026	Mainly intergranular, 0.5–20 $\mu$
7	95.0	4.9	0.1	0	0	4	0.042	Intergranular, mainly 1 $\mu$
8	98.3	1.0	0.5	0.1	0.1	3	0.020	Intergranular, mainly 0.5 $\mu$
9	39.8	33.7	24.2	1.9	0.4	13	0.018	Mainly intergranular, 0.5–20 $\mu$
10	0	0	0	0	100	1000	0.000	Intragranular (trace), $\leq 1 \mu$
11	100	0	0	0	0	1 <sup>a</sup>	0.89 <sup>b</sup>	Intergranular, wide size range

<sup>a</sup> Estimate by electron microscopy.

<sup>b</sup> By mercury intrusion.

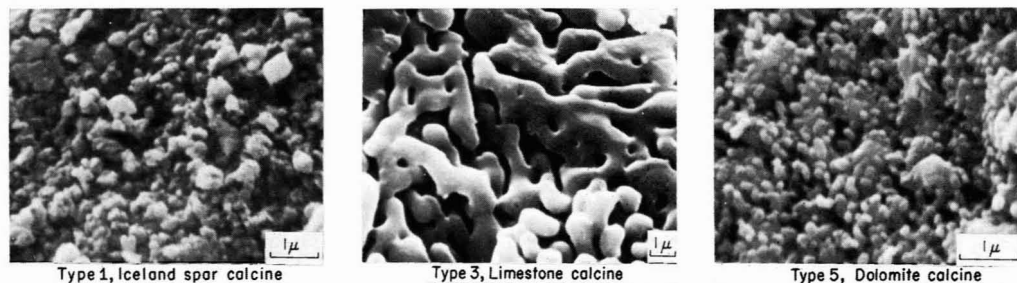


Figure 2. Typical surface textures of calcined carbonate rocks

rate of the larger particles to the initial rate of the smallest particles.

Total CaO utilization, or the nominal  $\text{SO}_2$ -saturation capacity, was determined for each particle size by exposure for 2 hr at  $980^\circ\text{C}$ .

### Results

**Petrography of Carbonate Rocks.** Identification of the rock types is given in Table I, along with a description of their major mineral components. With the exception of rare and exotic varieties, the complete spectrum of naturally occurring carbonate rocks was represented in this group. Variations in textural features were pronounced, as shown by SEM micrographs of typical specimens (Figure 1). The primary textural features, observed from microscopic analyses, are summarized in Table I. The grain size frequency distribution, mean grain size, pore volume, and pore characteristics are given in Table II.

Pore volume and grain size distribution are believed to be the primary characteristics of the rock that influence the pore structure and reactivity of the calcine. Complete chemical analyses of both major and minor elements were also made. These, together with detailed mineralogical descriptions of each rock type, are reported elsewhere (Harvey, 1970).

**Physical Properties of Calcines.** The calcination of calcium carbonate particles at temperatures below  $1100^\circ\text{C}$  generally takes place without significant change of particle dimensions. This fact, together with the difference in absolute density between  $\text{CaCO}_3$  (2.71 g/cc) and CaO (3.32 g/cc), defines a specific volume of 0.660 cc/g for the calcined product when no shrinkage occurs. The corresponding theoretical pore volume is 0.36 cc/g, which makes more than half the total particle volume free pore space. The resulting spongy texture of the calcines is shown clearly with the SEM (Figure 2). Quantitative characterization of the pore structure of each calcine was made by mercury intrusion and BET surface area measurements, summarized in Table III. Most measured pore volumes were close to 0.36 cc/g, confirming that shrinkage was not significant. The large pore volume of the marl reflects the unconsolidated nature of the starting material, which had a pore volume of 0.89 cc/g prior to calcination.

Type 1, and more particularly Type 10, both highly crystallized rocks, yielded calcines of low pore volume, indicating shrinkage when calcined at  $980^\circ\text{C}$ . The coarseness of the calcite grains and possibly the perfection of the crystals apparently contribute to shrinkage and low pore volume in the calcined product. This observation is in agreement with the results reported by others who have compared the shrinkage of coarse-grained and fine-grained limestones during calcination (Boynton, 1966). Type 1 was therefore calcined at a re-

Table III. Summary of Physical Properties of Calcines

Sample type no.	Mean pore diam, <sup>a</sup> $\mu$	Pore volume, <sup>a</sup> cc/g	BET surface, <sup>b</sup> $\text{cm}^2/\text{g} \times 10^{-4}$
1	0.075	0.25	10.2
2	2.1	0.30	0.7
3	0.60	0.29	1.8
4	0.44	0.32	2.4
5	0.27	0.42	3.9
6	0.30	0.40	4.1
7	0.01	0.34	37.8
8	4.0	0.36	0.8
9	0.42	0.36	3.7
10	0.065	0.032	0.6
11	1.6	1.21	2.2

<sup>a</sup> By mercury intrusion excluding voids  $>1 \mu$ . Voids  $>10 \mu$  excluded on Types 2, 8, and 11.

<sup>b</sup> Mean particle diam = 0.0096 cm.

duced temperature of  $930^\circ\text{C}$  for reactivity testing. Comparing the data of Tables II and III suggests that the initial porosity of the rock is not destroyed by the calcination process, but is carried through to yield calcines of higher than theoretical pore volume.

The data of Table III show marked differences between the properties of calcines prepared from the various types of rock, the most striking being the size of the pores, which range from 0.01 to  $4 \mu$  in diam.

The pore structure of a given calcine showed no dependence on the size of the screened particles, as determined by either mercury porosimetry measurements or SEM examination. The smallest, 0.01-cm particles, had surface areas slightly greater than the largest, 0.13-cm particles. The difference, about  $0.4 \text{ m}^2/\text{g}$ , is assumed to result from the new surface exposed at the points of fracture when the solid is crushed to make small particles.

**Reactivity with  $\text{SO}_2$ .** Reactivity of the smallest particles of the various calcined stones when exposed to flue gas at  $980^\circ\text{C}$  is shown in Figure 3. The marble and spars reacted slowly, whereas the marl and dolomites were the most reactive. The saturation capacities of each particle size and primary kinetic parameters are given in Table IV. Activation energies, measured at a sulfation of  $10^{-3} \text{ g-mol/g}$ , were in the range previously reported.

Type 7, a magnesite, showed no  $\text{SO}_2$  sorption beyond that attributable to CaO impurities at any reaction temperature between  $540^\circ$  and  $980^\circ\text{C}$ . Additional tests were made by calcining 0.0096-cm rock particles in situ at reaction tem-

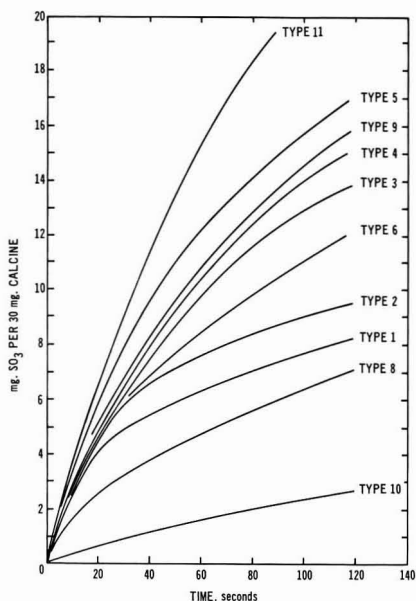


Figure 3. Comparison of reactivity of calcines with  $\text{SO}_2$  at  $980^\circ\text{C}$   
Particle size =  $0.0096\text{ cm}$ ;  $\text{SO}_2 = 3000\text{ ppm}$

perature—i.e., rock particles were placed on the reactor carrier and inserted into the heated reactor to calcine immediately prior to  $\text{SO}_2$  exposure. The maximum reactivity was found at  $650^\circ\text{C}$ , at which  $6.5\text{ mg}$  of  $\text{SO}_2$  were absorbed by  $30\text{ mg}$  of calcine in  $100\text{ sec}$ . At  $760^\circ\text{C}$ , sorption dropped to  $2.6\text{ mg}$  per  $100\text{ sec}$  exposure. At  $540^\circ\text{C}$ , as at  $980^\circ\text{C}$ , only  $1\text{ mg}$  of  $\text{SO}_2$  was absorbed.

The capacities of Type 1 (Iceland spar) and Type 10 (calcitic marble) were especially sensitive to particle size, CaO utilization increased by a factor of two when particle size was reduced from  $0.13$  to  $0.025\text{ cm}$ , and increased again by a factor of three when particle size was reduced from  $0.025$  to  $0.0096\text{ cm}$ .

The rate of  $\text{SO}_2$  sorption was dependent on the particle size of the calcine for all stones except the aragonite and marl. The sensitivity of rate to changes in particle size was different for each calcine, as illustrated in Figure 4 for two mineralogically and chemically similar limestones. Correlation of data on particle size and sulfation was made graphically according to Equation 3 as shown in Figure 5. The exponential decay of reaction rate with sulfation was typical of all calcines and was valid to about  $50\%$  CaO conversion in small particles. The slope of the line in this linear region,  $\beta$ , was a strong function of particle size—i.e., the rates dropped more rapidly for large particles than for smaller particles. The value of  $\beta$  was also a function of pore size and stone type. This coefficient was therefore tabulated for comparison in Table IV.

Values of  $r_0$  given in Table IV were obtained by extrapolation of the rate data to zero sulfation (Figure 5). The tabulated effectiveness factors were estimated as the ratio of the initial rate of the larger particles to that of the finest particle size,  $r_0^*$ . This assumes  $\eta \approx 1$  for  $\bar{D}_p = 0.0096\text{ cm}$ , which appears to be justified by the experimental evidence for all stones except Types 1 and 10, as discussed later. The reaction rate constants in Table IV were computed from  $r_0^*$  by means of

Equation 2 using the BET surface area of the unreacted calcine (Table III).

Values of the effectiveness factor estimated by the above method for  $0.025\text{-cm}$  particles at  $980^\circ\text{C}$  are plotted against the pore size of the calcines in Figure 6. It is apparent that  $\eta$  is strongly dependent on pore size for pores smaller than  $0.7\text{ }\mu$ , reflecting the increasing resistance of pore diffusion.

#### Discussion

**Reaction Rate.** The  $\text{SO}_2$  reaction characteristics of the calcined stones are primarily affected by the relation between pore size and the effectiveness factor shown in Figure 6. As particle size was varied, three distinct responses in reaction rate were obtained for calcines prepared from the 11 different types of rock. These responses are represented in Figure 7 by (1) a curve approximating a straight line through the origin, (2) a horizontal line, and (3) an exponential curve. The form of the response of any given calcine depended on the size of its pores. Most stones, which had intermediate-sized pores in the range  $0.2\text{--}0.7\text{ }\mu$ , followed the first type of response. This defines pore diffusion as the predominant resistance that limits the rate of  $\text{SO}_2$  sorption by the larger particles (Satterfield and Sherwood, 1963).

As shown by Figure 6,  $\eta$  drops sharply for  $0.025\text{-cm}$  particles that have pores smaller than  $0.7\text{ }\mu$ , indicating reduced penetration of the particle interior by  $\text{SO}_2$  until, when  $\eta \ll 1$ , the reaction is confined to the outside periphery of individual particles and only the superficial surface participates in the reaction. Since this superficial area increases directly with  $1/\bar{D}_p$  for a given mass of solid, so also will the reaction rate. This effect is illustrated in Figure 7 by the data for Type 9, which show the linear increase in rate for particle sizes down to  $100/115$  mesh. When these particles were reduced from  $100/115$  to  $150/170$  mesh, the rate did not increase further, indicating a change from pore diffusion to chemical reaction as the predominant resistance ( $\eta = 1$ ).

Calcines with the largest pores, Types 8 and 11 ( $\eta = 1$ , Figure 6), showed rates independent of particle size for all values of  $\bar{D}_p$  (horizontal line, Figure 7). This response indicates that pore diffusion imposes no significant resistance to  $\text{SO}_2$  sorption for these calcines, and reaction occurs evenly throughout their pore structure. The rate of  $\text{SO}_2$  sorption in this case (as for the smallest particles of Type 9) is determined solely by chemical reaction rate.

The third type of response, shown as an exponentially rising curve in Figure 7, was found for calcines with the smallest pores, Types 1 and 10. This high sensitivity to particle

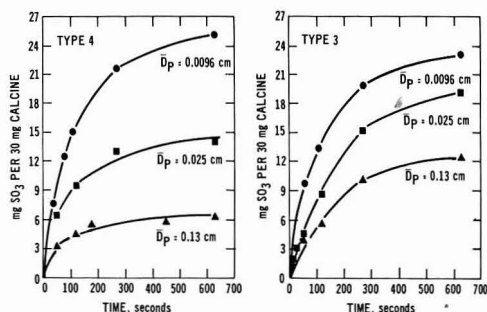


Figure 4. Effect of particle size and pore size on sorption of  $\text{SO}_2$  vs. time by calcines of coarse-grained (Type 3) and fine-grained (Type 4) limestones

$\text{SO}_2 = 3000\text{ ppm}$



Table IV. Parameters for SO<sub>2</sub> Sorption by Calcines as a Function of Particle Size at 980°C

Sample type no.	Mean particle diam, cm	Initial rate, $r_0 \times 10^4$ g-mol/g CaO-sec	Reaction rate constant, $k_s$ cm/sec	Initial effectiveness factor, $\eta$	$\beta \times 10^{-2}$	Total capacity <sup>a</sup>	Total CaO utilization <sup>b</sup>
1	0.13	0.0092	0.190	<0.0018	25.4	2.6	6.2
	0.025	1.06		<0.21	30.4	6.0	13.6
	0.0096	5.01		13.4	18	43	
2	0.13	0.280	0.755	0.17	12.3	17	40
	0.025	1.44		0.85	10.5	18	43
	0.0096	1.65		7.8	21	50	
3	0.13	0.710	0.241	0.62	6.62	20	49
	0.025	0.895		0.79	3.83	25	64
	0.0096	1.14		2.77	33	80	
4	0.13	0.673	0.227	0.47	12.5	6.8	16
	0.025	1.06		0.74	4.80	18	43
	0.0096	1.44		2.89	33	80	
5	0.13	1.06	0.324	0.32	17.9	9.0	37
	0.025	1.63		0.49	3.93	22	90
	0.0096	3.32		3.03	22	90	
6	0.13	0.437	0.153	0.27	4.58	19	100
	0.025	1.03		0.63	3.00	19	100
	0.0096	1.63		1.92	19	100	
8	0.025	0.324	0.156	1	2.38	36	86
	0.0096	0.324			2.38	39	93
9	0.13	1.02	0.212	0.49	6.18	17	75
	0.025	1.33		0.64	2.65	24	100
	0.0096	2.10		2.05	24	100	
10	0.13	0.527	(nonporous solid)			2.0	4.9
	0.025					4.8	11.7
	0.0096					14.3	35
11	0.13	1.00	0.181	1	2.14	35	100
	0.025	1.00		1	2.14	35	100
	0.0096	1.00		2.14	35	100	

<sup>a</sup> Milligrams SO<sub>2</sub> absorbed by 30 mg calcine, 2-hr exposure.

<sup>b</sup> % conversion of CaO to CaSO<sub>4</sub>, 2-hr exposure.

size would be expected for diffusion through a product shell, which surrounds nonporous particles, as the rate-limiting resistance where

$$r \propto \frac{1}{D_p^2}$$

This is easily shown by writing the equation for product layer diffusion, such as Equation 31 of Shen and Smith (1965), in terms of conversion and differentiating implicitly. The curve for Type 1 calcine in Figure 7 actually indicates a greater sensitivity to particle size than predicted by the above equation. This is probably due to a reduced permeability of the shell formed on the larger particles which, to obtain equal conversion, were reacted for longer periods than small particles. The CaO grains within the product shell will achieve greater conversion and expansion at longer reaction periods.

The reaction mechanisms inferred from the effects of particle size and pore size on the reaction rate were confirmed

by electron microprobe analysis of the sulfur (as sulfate) distribution within individual reacted particles. Figure 8A shows the distribution over a cross section of Types 1 and 10 calcines, where sulfate was present only at the outer surface of particles exposed to SO<sub>2</sub> for 10-120 min. Line scans across calcines of Type 3, exemplified by Figure 8B, show the presence of sulfate throughout the porous particles; however, in most particles, a slight enrichment of sulfate occurs on the outer edge. The sulfate located in the interior of the particle is interpreted to occur on the surface of the pores or interstices between the lime grains observed by SEM (Figure 2). Calcines of the marl (Type 11) and oolitic aragonite (Type 8), both of which have SO<sub>2</sub> reaction rates independent of particle diameter (horizontal curve, Figure 7), contained sulfate throughout the interior of the particles (Figure 8C). No evidence of increased sulfate content on the outer surface of these particles was observed. As in Type 3, the sulfate is distributed throughout the internal surface of the lime particles.

It was concluded from these results that pore size determines the extent to which the internal structure of large particles participates in the  $\text{SO}_2$  reaction. As particle size is reduced or pore size is increased, the effect of pore diffusion diminishes ( $\eta \rightarrow 1$ ) until chemical reaction becomes the sole rate-limiting resistance for small particles. For the smallest particle size, where the effectiveness factor is unity, Equations 2 and 3 indicate that a linear relationship should exist between reaction rate and BET surface area when comparing initial rates of stones with equal values of  $k_s$ , or when comparing rates at a given conversion for stones with equal values of  $\beta$ . The reaction rates of 0.0096-cm particles, measured at a sulfation of  $2.9 \times 10^{-3}$  g-mol  $\text{SO}_2/\text{g}$  calcine, are plotted in Figure 9 for those calcines with similar  $\beta$  values shown in Table IV. The linear correlation of reaction rate with surface area confirms the predominant influence of chemical reaction on  $\text{SO}_2$  sorption that was previously inferred from activation energy and particle size effects.

Included in Figure 9 is a datum obtained from the in situ calcination of marl. All rock types were tested in this manner, but only the marl showed significant difference in reactivity

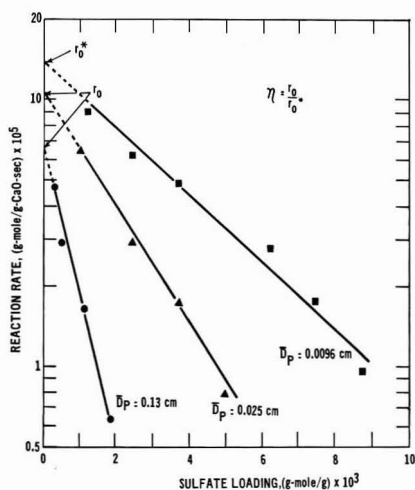


Figure 5. Estimation of initial rate,  $r_0$ , and initial effectiveness factor,  $\eta$ , for sorption of  $\text{SO}_2$  by Type 4 calcine

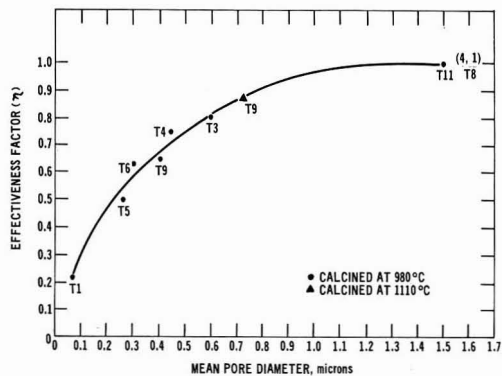


Figure 6. Relationship between effectiveness factor at initial conditions and pore size for 0.025-cm particles at  $980^\circ\text{C}$

compared to the calcines prepared in the rotary kiln. The data also include two samples calcined at  $1110^\circ\text{C}$  representing the effect of reduced surface area. The reaction rate of the dolomites, Types 5 and 9, correlates well with that of limestones when the rate is expressed in terms of CaO content, as shown in Figure 9. This is explained by the peculiar structure of the calcined dolomites (Type 5, Figure 2), in which the CaO is crystallized as very small grains attached to the surface of much larger MgO grains. The MgO consequently contributes little to the surface area and the BET measurements essentially represent the surface area of the CaO component only. Not plotted in Figure 9 was Type 6, with a rate of  $8.5 \times 10^{-5}$  g-mol/g CaO (sec). The low reaction rate of this dolomite is attributed to its high content of impurities, which compose 23 wt % of the calcine. The BET measurement does not, therefore, accurately represent CaO surface in this case.

The general correlation of reaction rate with the BET surface area of different calcined stones shown in Figure 9 was confirmed for the specific case by altering the pore structure of a single stone. The effect of calcination temperature on the surface area of the calcine has been established (Chan et al., 1970); surface decreases with increasing temperature—with a corresponding enlargement of pore size. Type 4 limestone was calcined at its minimum dissociation temperature ( $790^\circ\text{C}$ ) at atmospheric pressure, and three additional calcinations were made at  $890^\circ$ ,  $980^\circ$ , and  $1100^\circ\text{C}$ . The surface area of each calcine was measured and the  $\text{SO}_2$  sorption rate of 0.0096-cm particles determined at a reaction temperature of  $760^\circ\text{C}$ . The results, shown in Figure 10, demonstrate the strong influence of surface area on the rate of reaction.

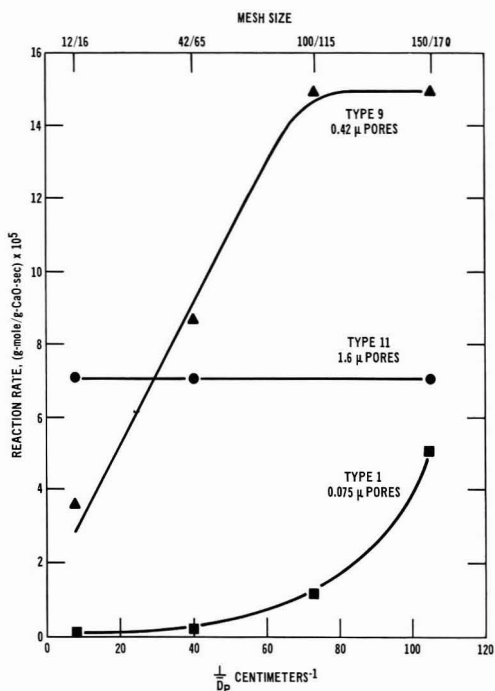


Figure 7. Reaction rate at constant sulfation as affected by the pore size of the calcine, illustrating zero, linear, and exponential responses to  $1/\bar{D}_p$

Sulfation =  $1.67 \times 10^{-3}$  g-mol  $\text{SO}_2/\text{g}$  calcine

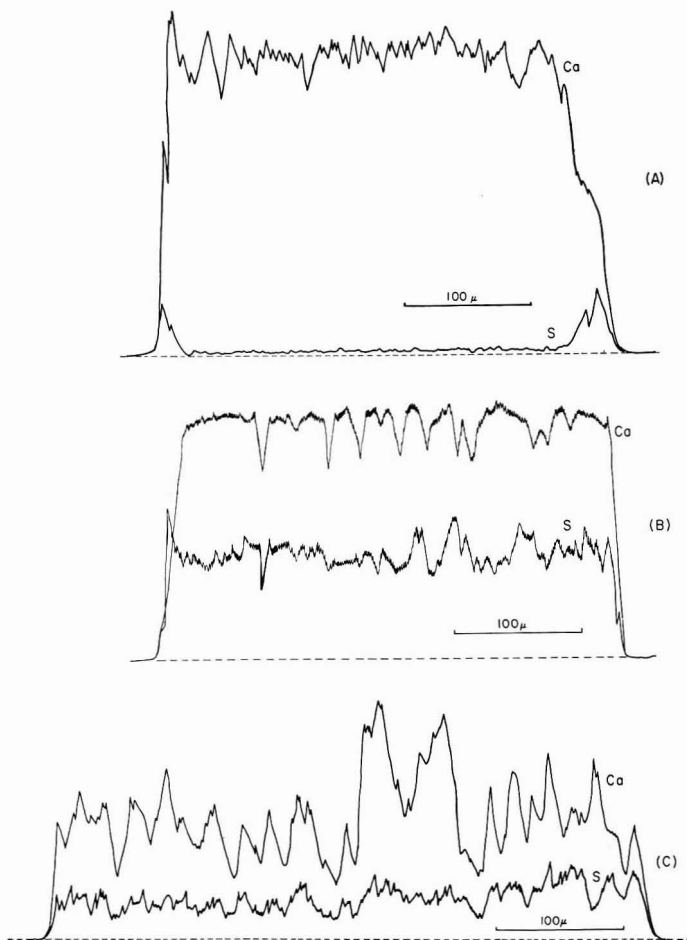


Figure 8. Microprobe line scans of reacted particles

(A) 0.025-cm Iceland spar calcite, Type 1, exposed to  $\text{SO}_2$  for 120 min; (B) 0.025-cm calcine of limestone, Type 3, exposed for 120 min; (C) 0.048-cm marl, Type 11, exposed for 10 min. (A) Shell reaction with  $\text{SO}_2$ ; (B) and (C) volumetric reaction

The data of Table IV indicate that the reaction rate constant per unit CaO surface is of similar magnitude for most of the calcines tested. The intrinsic reaction rate constant can be estimated as the average of the  $k_s$  values for stone Types 1, 3, 4, 5, 8, 9, and 11 at  $980^\circ\text{C}$ :

$$\bar{k}_s = 0.22 \pm 0.05 \text{ cm/sec}$$

The only significant deviation from this average was Type 2; its high rate constant probably is related to the presence of large concentrations of crystalline imperfections in the original rock.

The effect of the BET surface on the reaction rate provides a clear basis for explaining the anomalous, transient reaction rates on which the limestone injection process appears to be based (Borgwardt, 1970b). The existence of very large surface areas immediately following the dissociation of  $\text{CaCO}_3$  was postulated (Mayer and Stowe, 1964) from considerations of the molecular rearrangements that must occur within unit crystal cells when CaO is formed. Recent measurements of surface areas of calcines prepared under boiler injection conditions—i.e., small particles calcined in periods of less than 3 sec in dispersed systems, have been reported (Ishihara, 1970; Coutant, 1970) to be an order of magnitude greater than those of calcines prepared at the same temperature ( $980^\circ\text{C}$ ) by the

technique used in this study. The initial rates of the stones having similar  $k_s$  values indicated above are compared in Figure 11 with the data reported by Coutant (1970) for reaction in a dispersed-phase reactor. The triangles are the initial rates obtained from the data of Figure 10 normalized to  $980^\circ\text{C}$  on the basis of the measured activation energy (12,500 cal/g-mol) for Type 4 limestone. Coutant's data (circles) represent the average of 10 BET measurements on 0.0090-cm limestone particles injected into a reactor for residence times ranging from 0.15 to 2.86 sec. A linear relationship, corresponding to chemical reaction control, correlates the initial rate with BET surface for both reactors. This agreement supports Ishihara's conclusion that mass transfer of  $\text{SO}_2$  to the particle surface does not limit the rate of  $\text{SO}_2$  sorption in the dispersed system.

**Reaction Capacity.** The direct relationship between reaction rate and the BET surface area shown in Figure 9 suggests that calcines of small pore size will have the highest rate of reaction, since the total pore surface of a given mass of calcine is inversely proportional to the pore diameter or CaO grain size (Mayer and Stowe, 1964). The increase in reaction rate with decreasing pore size will be valid as long as the effectiveness factor remains unity. The strong influence of pore size on the value of  $\eta$  (Figure 6) will, however, impose a limit on this

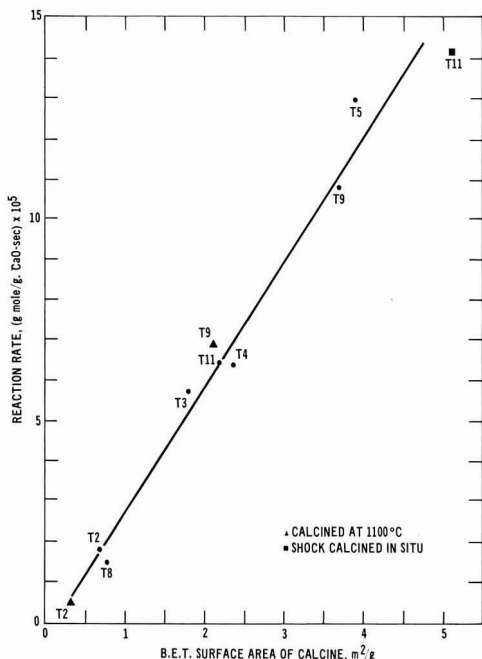


Figure 9. Reaction rate vs. surface area of 0.0096-cm particles  
Rates evaluated at 980°C,  $2.9 \times 10^{-3}$  g-mol/g calcine;  $\text{SO}_2 = 3000$  ppm

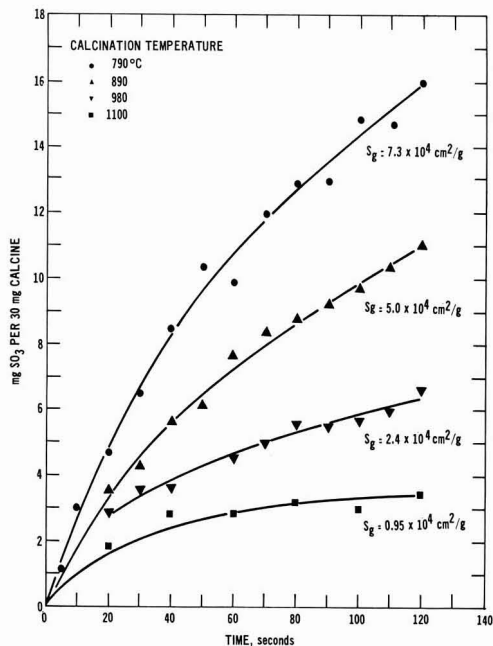


Figure 10. Sorption of  $\text{SO}_2$  by Type 4 limestone as a function of surface area of its calcine

Reaction temp = 760°C; particle size = 0.0096 cm;  $\text{SO}_2 = 3000$  ppm

relationship for any given particle size. Reduced values of the effectiveness factor for small pores, in addition to indicating inaccessibility of interior particle surface to  $\text{SO}_2$ , will also have an important bearing on the ultimate capacity for  $\text{SO}_2$  sorption as the reaction progresses.

If an individual pore is idealized as a cylinder, the surface/volume ratio of that pore will increase linearly as pore diameter becomes smaller. Thus, the capacity to accumulate product decreases relative to the rate of product generation within the reaction zone of the pore. Carrying this reasoning to conclusion, one would expect a maximum specific reaction rate and minimum reaction capacity with very fine pores, which would result in the plugging of the pore mouths with reaction product. The data for Type 1 (pore diam =  $0.07 \mu$ ,  $S_p = 10^5 \text{ cm}^2/\text{g}$ ) show this effect clearly. Both the reaction rate and the reaction capacity of this calcine were highly sensitive to particle size, suggesting that the reaction was confined to the outermost particle surface. Microprobe data (Figure 8.4) confirm the presence of a  $30\text{-}\mu$  thick product shell on these particles. Comparison of Type 1 calcine with the other calcines shows the effect of increased pore size (and  $\eta$ ) on the capacity. Capacity (Table IV) of the 0.025-cm particles of limestone increases in the same progression as pore size

$$T_{10} < T_1 < T_4 < T_3 < T_2 < T_8$$

The effect of pore size on the reactivity of different particle sizes of calcines is demonstrated in Figure 4, which shows  $\text{SO}_2$  sorption by three particle sizes of Type 3 (pore diam =  $0.6 \mu$ ) and Type 4 (pore diam =  $0.4 \mu$ ). Large particles of Type 3, which has the bigger pores, are more reactive than large particles of Type 4. As particle size is reduced and  $\eta \rightarrow 1$ , the reactivity becomes increasingly a function of chemical reaction rate so that when the finest particles are compared, the calcine with the smallest pores (and greatest BET surface), Type 4, becomes the most reactive. These effects are consistent with the general observations discussed with regard to Figure 7 which covers a broader range of pore sizes.

When the effectiveness factor is unity (small particles, large pores, or both) the reaction occurs at an even rate throughout the pore structure of individual particles, and the entire pore volume fills with reaction product. The total capacity in this

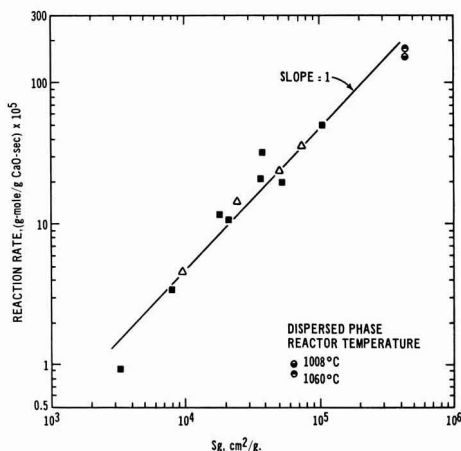


Figure 11. Comparison of initial  $\text{SO}_2$  reaction rates in differential reactor (980°C,  $\bar{D}_p = 0.0096$  cm) and dispersed-phase reactor

$\text{SO}_2 = 3000$  ppm

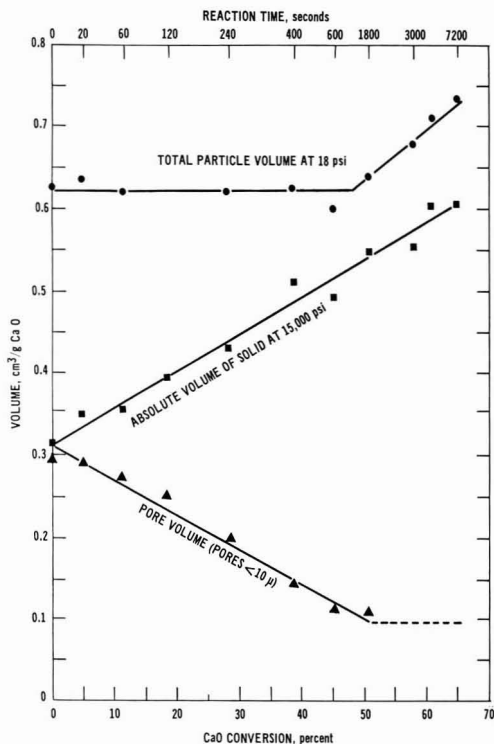


Figure 12. Pore volume and particle volume as a function of conversion in 0.025-cm particles, Type 3 at 980°C

case is dictated for limestones by the limit defined by the difference in specific volume of the calcine particle and the reaction product. Thus, if no particle expansion occurs:

$$\text{vol CaSO}_4 \text{ formed} = \text{pore vol} + \text{vol CaO reacted} \quad (4)$$

This relationship was demonstrated by mercury intrusion measurements on samples of Type 3 limestone reacted to varying degrees of sulfation in the differential reactor. The degree of conversion of CaO to CaSO<sub>4</sub> in each sample was determined and its pore volume measured in a porosimeter. The results, given in Figure 12, show a progressive decrease in the volume of pores as sulfation increased. The particle volume (measured at 18 psi, at which pressure the mercury does not penetrate the pores) remained constant until the solid conversion reached about 50%. The difference between the particle volume and the absolute volume of the solid (measured at 15,000 psi, at which pressure the pores are completely filled by mercury) decreases as solid conversion progresses. This clearly shows the accumulation of the reaction product in the internal pore structure of the particles. Only when the conversion reached a level corresponding to essentially complete filling of the available pore volume (49% conversion according to Equation 4) did the particles begin to expand in accordance with the change in specific volume between CaO and CaSO<sub>4</sub>. At this point, indicated in Figure 12 by the sharp upward break in particle volume, further SO<sub>2</sub> sorption can occur only through the exterior surface of the particles. This conversion also coincides with the sharp break in reaction rate from the exponential decay which characterizes the pore filling stage. The reduced rate at conversions exceeding 50% presumably re-

sults from a change in the rate-controlling mechanism from chemical reaction in the pores to diffusion through the solid.

The high reaction capacity of the dolomites (100% CaO conversion) is accounted for by the relationship given by Equation 4. The ratio of pore volume to CaO content is about twice that of limestone, providing adequate space to accommodate the entire reaction product without particle expansion. Porosimetry measurements were made on samples of Type 9 dolomite calcine reacted to 50, 75, and 100% CaO conversion and showed no change in particle volume from that of the unreacted calcine.

### Conclusions

The observed variations in reactivity among limestones can be explained by differences in the physical properties of their calcined products. The size of the pores developed by calcination has a critical effect on the rate and ultimate capacity for SO<sub>2</sub> sorption. Small pores result in a high reaction rate, but if the particles are large, their capacity is low. Large pores give lower rates and increased capacities. The capacity of small particles, in which reaction occurs evenly throughout the pore structure under isothermal conditions of reaction, is determined by the total pore volume available for accumulation of the reaction product.

When pores are larger than 0.1 μ, chemical reaction is the sole resistance limiting SO<sub>2</sub> sorption by particles smaller than 0.01 cm at temperatures up to at least 980°C, and CaO conversions to 50%.

The specific reaction rate of small particles increases in direct proportion to their BET surface area. The intrinsic reaction rate constant of SO<sub>2</sub> with CaO derived from different carbonate rocks is approximately the same, 0.22 cm/sec, when evaluated on the basis of surface area at zero conversion. At conversions greater than 50%, the pores of small particles are completely filled with CaSO<sub>4</sub> and the rate-limiting mechanism changes from chemical reaction to solid diffusion.

The nature of the original rock affects the properties of its calcine. Although too few samples were examined to establish quantitative relationships, several general trends were apparent. First, the porosity of the rock is carried through the calcination process to yield products of higher-than-theoretical pore volume. Second, the more coarse-grained and perfect crystalline rocks appear to develop the finest pore structures, which can plug quickly with CaSO<sub>4</sub>. Highly crystallized rocks also tend to show greater differences between theoretical and observed pore volumes, even under mild calcination conditions. Third, reaction of SO<sub>2</sub> with calcines prepared from very fine-grained, highly microporous, and incoherent carbonate rocks is less sensitive to the degree of sulfation. Compared at a given conversion and particle size, the reaction rate of limestones and marl decreased with the petrographic grain size. Large perfect rhombs of Iceland spar calcite and the calcitic marble produced anisotropic lime when calcined at 980°C. These observations suggest that the presence of imperfections and grain boundaries in crystalline rocks tends to enhance their reactivity, possibly by facilitating the conversion from anisotropic calcite to isotropic lime during calcination.

Magnesia reacts slowly with SO<sub>2</sub> at any temperature between 540° and 980°C under isothermal conditions. The high reactivity of dolomites is due to the small grain size of the CaO component, which crystallizes independently from MgO during calcination. This structure results in a large CaO surface area and provides sufficient pore volume to accommodate the 173% expansion that occurs when individual CaO grains

are converted completely to  $\text{CaSO}_4$  without closing the pore structure to  $\text{SO}_2$  diffusion.

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#### Nomenclature

$C_{\text{SO}_2}$  = gas-phase concentration of  $\text{SO}_2$ , g-mol/cc  
 $\bar{D}_p$  = mean particle diam, cm  
 $f$  = weight fraction of CaO in calcine  
 $k_s$  = reaction rate constant per unit CaO surface, cm/sec  
 $k_v$  = reaction rate constant per unit volume of calcine,  $\text{sec}^{-1}$   
 $n'$  = sulfate in solid as  $\text{SO}_3$ , g-mole  
 $r$  = rate of formation of  $\text{SO}_3$  in solid, g-mol/g CaO (sec)  
 $r_0$  = initial rate at zero conversion, g-mol/g CaO (sec)  
 $r_0^*$  = initial rate for smallest-sized particles, g-mol/g CaO (sec)  
 $S_g$  = BET surface area of calcine,  $\text{cm}^2/\text{g}$   
 $W$  = weight of calcine sample, g  
 $t$  = time, sec

#### GREEK LETTERS

$\beta$  = empirical coefficient defined by Equation 3  
 $\eta$  = effectiveness factor, ratio of reaction rate to rate that would be obtained if entire volume of particle par-

icipated equally in reaction

$\rho_p$  = bulk density of calcine (particle density), g/cc

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## Analytical Studies of Simplified Photochemical Smog Kinetics

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■ Analytic solutions have been obtained for the relationships between pollutant concentrations in the Friedlander-Seinfeld simplified model of the kinetics of photochemical smog. Time is then related to the NO concentration, and hence to the other reactants, by a quadrature. From these results, approximate representations for the temporal dependence of reactants are obtained for short and long times. Important dimensionless groupings are identified which control the buildup and rate of decay of reactants. Relaxation times to achieve a steady state are determined from these results. A criterion for  $\text{NO}_2$  concentration to be a monotonic function of time is also established. Finally, results are presented for special values of the kinetic rate parameters. Comparisons are made between analytic results and numerical solutions. Comments on the applicability and usefulness of these results are included.

Considerable attention has been given to mathematical simulation of atmospheric rate processes. Because of the number of reactions, the models reduce generally to large systems of nonlinear ordinary differential equations. These systems contain a wide diversity of rate constants and characteristic reaction times making numerical integrations revealing the details of transient and long-time behavior difficult and time-consuming. Furthermore, no theory of general utility is available to establish the accuracy of integration schemes applied to such nonlinear systems. Thus, it is important to devise simplified analytical solutions to model systems to be used as milestones in development of useful, but complicated equations for realistic reaction schemes.

Evidence has been given that the basic features of smog chemistry may be accessible to sets of equations of consider-

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ably lower order than those accounting for all of the intricacies of the production of intermediate species, such as free radicals. Solutions of such reduced or simplified systems then become accessible analytically. Such solutions have important advantages over numerical results in the sense that they more clearly show the parametric dependence of the reactants, and they allow the investigator to readily predict the buildup and decay of the species. They also enhance the development of analytical solutions of convection models that incorporate chemical reaction mechanisms, or boundary conditions by introduction of analytically tractable chemical rate models.

In this paper, one example of such a simplified system will be treated to illustrate the use of well-known techniques of analysis in deriving significant results about the properties of interdependent chemical reactions. The model used for this study has been proposed by Friedlander and Seinfeld (1969). We have observed that their system of equations can be solved to give closed-form relationships between concentrations of the reactants. This is true not only for their final set of equations but also for their system with one assumption removed. In this paper, our analysis for solutions of their final set is presented and applied to obtain results of the type described above.

#### Kinetic Model

Friedlander and Seinfeld started with a set of six coupled differential equations and made various approximations to reduce them to the following system:

$$\frac{d(\text{NO}_2)}{dt} = (\text{NO}_2)(\text{RH})[\alpha(\text{NO}) - \lambda(\text{NO}_2)] \quad (1a)$$

$$\frac{d(\text{NO})}{dt} = -\alpha(\text{NO}_2)(\text{NO})(\text{RH}) \quad (1b)$$

$$\frac{d(\text{RH})}{dt} = -(\text{NO}_2)(\text{RH})[\theta + \mu/(\text{NO})] \quad (1c)$$

Here the original notation is retained with  $\alpha$ ,  $\lambda$ ,  $\theta$ , and  $\mu$  given in terms of the rate constants for the seven reactions comprising the model.

As an extension of the work of Friedlander and Seinfeld, we have obtained a separated form of the equations by using Equation 1b to reexpress 1a and 1c in terms of NO rather than  $t$  as the independent variable. The resulting expressions are:

$$\frac{dA}{dB} = r \frac{A}{B} - \frac{1}{\nu} \quad (2a)$$

$$\frac{dC}{dB} = \frac{\kappa}{B} + \frac{\delta}{B^2} \quad (2b)$$

where

$$A \equiv \frac{(\text{NO}_2)}{(\text{NO}_2)_0}, B \equiv \frac{(\text{NO})}{(\text{NO})_0}, C \equiv \frac{(\text{RH})}{(\text{RH})_0}, \nu \equiv \frac{(\text{NO}_2)_0}{(\text{NO})_0} \quad (2c)$$

$$\delta \equiv \frac{\mu}{\alpha(\text{NO})_0(\text{RH})_0}, \kappa \equiv \frac{\theta}{\alpha(\text{RH})_0}, \rho \equiv \frac{1}{\nu} \left( \frac{1}{1-r} \right), r \equiv \frac{\lambda}{\alpha} \quad (2d)$$

with  $(\text{NO}_2)_0$ ,  $(\text{NO})_0$ , and  $(\text{RH})_0$  signifying the values of  $(\text{NO}_2)$ ,  $(\text{NO})$ , and  $(\text{RH})$  at  $t = 0$ . Equations 2 may be easily integrated giving the concentrations in normalized form:

$$A = (1 + \rho)B^r - \rho B \quad r \neq 1 \quad (3a)$$

$$= B \left( 1 - \frac{\ln B}{\nu} \right) \quad r = 1$$

$$C = 1 + \delta \frac{(B-1)}{B} + \kappa \ln B \quad (3b)$$

Substitution of Equations 3 into Equation 1b gives the time normalized as shown, expressed as a quadrature of the NO concentration.

$$\tilde{t} \equiv \frac{t}{\tau} = \frac{1}{\rho} \int_B^1 \frac{dx}{x^2(Dx^{r-1} - 1) \left[ 1 + \delta \frac{(x-1)}{x} + \kappa \ln x \right]} \quad (4)$$

where

$$\tau \equiv \frac{1}{\alpha(\text{NO}_2)_0(\text{RH})_0} \text{ and } D \equiv \frac{1 + \rho}{\rho} = 1 + \nu(1-r)$$

The parameter  $r$  is just the ratio of the rate constants for free radical reactions with the  $\text{NO}_2$  and  $\text{NO}$ , respectively. The first is the chain-terminating reaction and the second, the chain-propagating reaction. The relationship between the normalized  $\text{NO}_2$  and  $\text{NO}$  concentrations given in Equation 3a depends only on the chain parameter  $r$ , and  $\nu$  on the ratio of the initial  $\text{NO}_2$  and  $\text{NO}$  concentrations. The value of  $r$  obtained from the adjusted parameters of Friedlander and Seinfeld is 0.2. Since the free radicals involved in such mechanisms as this have not been identified, the actual ratio of rates can only be estimated. From Equation 1b,  $(\text{NO})$  monotonically decreases with time, and  $\tau$  will be its initial relaxation time.

We have integrated the set of Equations 1 numerically by use of a fourth-order Runge-Kutta method using Friedlander and Seinfeld's values for the various parameters, including initial concentrations. The results have been compared numerically to the solutions given in Equations 3 and 4. The integral Equation 4 was evaluated numerically using Simpson's Rule. In all of these comparisons, agreement within the accuracy of the numerical methods was obtained.

It is of interest to establish simple analytical relationships for the values in terms of the parameters of the system, of the peak  $\text{NO}_2$  concentration, the time at which it occurs, and the behavior of all of the concentrations for large and small times. These results can be obtained only by introducing certain approximations to make Equation 4 tractable. For this purpose, asymptotic methods will be employed (Bruijn, 1961; Cole, 1968; Erdélyi, 1956).

For practical cases,  $\delta$  and  $\kappa$  are small compared to unity. Accordingly, an approximation to Equation 4 may be formalized by considering a limiting case where  $\kappa = O(\delta)$  as  $\delta \rightarrow 0$  with  $B$  fixed. This condition will be valid for times such that the hydrocarbons have not reacted appreciably and is equivalent to assuming that they have not reacted at all. The resulting integral is:

$$\tilde{t} = \frac{1}{\rho} \int_B^1 \frac{dx}{x^2(Dx^{r-1} - 1)} \quad (5)$$

For  $|Dx^{r-1}| > 1$ , this integral has been treated by a binomial expansion which can be demonstrated to be uniformly convergent over this interval by the Weierstrass test. This property permits a subsequent term by term integration. The numerical values of the parameters used by Friedlander and Seinfeld

correspond to  $0 < B \leq 1$ ,  $0 \leq r < 1$ , and  $D < 1$ . Integration thus yields the following series representation for  $\tilde{t}$ :

$$D\tilde{t} = \frac{1}{\rho} \sum_{n=1}^{\infty} \frac{1 - B^{[n(1-r)-1]}}{[n(1-r) - 1]D^n} \quad (6)$$

For rational  $r$ , the integral in Equation 5 may be evaluated in closed form; or alternatively, Equation 6 may be summed. In particular for  $r = 0.2$  both yield:

$$\tilde{t} = \frac{5}{\rho} \left\{ \frac{1}{DB^{0.2}} - \frac{1}{D} + \frac{1}{4d^{0.5}} \left[ \log \left( \frac{B^{0.2} - d}{B^{0.2} + d} \frac{1+d}{1-d} \right) - 2 \tan^{-1} \left( \frac{d}{B^{0.2}} \right) + 2 \tan^{-1} d \right] \right\} \quad (7)$$

where

$$d \equiv D^{1/4}$$

Evaluation of Equations 6 and 7 for starting conditions given by Friedlander and Seinfeld gives 1% agreement with the numerical quadrature of Equation 3 for times up to 40 min, which is approximately twice the peak build-up time for  $\text{NO}_2$  with these starting conditions. Other approximations for  $r \rightarrow 0$  or  $\infty$  have also been obtained. The former leads to an asymptotic power series in  $r$  having coefficients which are dilogarithmic functions of the other parameters.

The concentrations of NO and  $\text{NO}_2$  and the time at the peak  $\text{NO}_2$  concentration may now be determined. The necessary condition for  $(\text{NO}_2)$  to have an extremum is that  $d(\text{NO}_2)/dt = 0$ . Substitution of this condition into Equation 1a yields:

$$(\text{NO}_2)_p = \frac{(\text{NO})_p}{r} \quad (8)$$

where the subscript  $p$  implies the value at the  $(\text{NO}_2)$  peak. A further substitution of Equation 9 into Equation 3a gives finally:

$$B_p \equiv \left[ \frac{(\text{NO})}{(\text{NO})_0} \right] = (rD)^{\frac{1}{1-r}} \quad (9)$$

for max  $(\text{NO}_2)$

For  $r \rightarrow 1$ , application of L'Hospital's rule gives  $B_p \rightarrow e^{\nu-1}$ . For  $r \rightarrow 0$ ,  $B_p \rightarrow r(1 + \nu)$ . An interesting result is obtained by noting that  $(\text{NO})$  is always a monotonically decreasing function of  $t$  for  $0 \leq t \leq \infty$  and the previously introduced normalizations in Equation 2c require  $B_p \leq 1$ . This implies that Equation 9 can be used to determine  $B_p$  only if  $\nu \leq 1/r$ . This ensures that the normalized time,  $\tilde{t}_p$  corresponding to the peak concentration of  $\text{NO}_2$  is positive. For  $\nu \geq 1/r$ ,  $(\text{NO}_2)$  has its maximum at  $t = 0$ , and hence is a monotonically decreasing function of time for  $0 \leq t \leq \infty$ .

It is significant at this point to note that the normalized time at which  $\text{NO}_2$  reaches its peak concentration and the value of the NO and  $\text{NO}_2$  concentrations both depend only on  $\nu$  and  $r$ . The parameter  $\nu$  is just the ratio of the initial concentrations of  $\text{NO}_2$  and NO, and  $r$  is the ratio of the rates of free radical reactions with  $\text{NO}_2$  and NO, respectively. When the  $\text{NO}_2$  concentration becomes large enough relative to the NO concentration the chains do not propagate and the  $\text{NO}_2$  is consumed to final products as fast as NO is converted to  $\text{NO}_2$ .

The value of  $\tilde{t}_p$  can be determined from substitution of

Equation 9 into Equation 6, or in the special case  $r = 0.2$ , Equation 7. For values of  $D$  near unity, this series does not converge rapidly, and manipulations such as Kummer's transformation (Knopp, 1948), can be used to accelerate its convergence. This is demonstrated in Appendix A.

To obtain the initial behavior as  $\tilde{t} \rightarrow 0$ , we introduce the substitution  $\xi = 1 - x$  in the integrand of Equation 5. Expansion of the integrand about  $\xi = 0$  and term-by-term integration gives a power series in the small parameter  $(1 - B)$

$$\tilde{t} = (1 - B) + O[(1 - B)^2] \quad (10)$$

which may be reverted to yield as  $\tilde{t} \rightarrow 0$ ,

$$\frac{(\text{NO})}{(\text{NO})_0} = B = 1 - \tilde{t} + O(\tilde{t}^2) \quad (11a)$$

$$\frac{(\text{NO}_2)}{(\text{NO}_2)_0} = A = 1 + (\nu^{-1} - r)\tilde{t} + \dots \quad (11b)$$

$$\frac{(\text{RH})}{(\text{RH})_0} = C = 1 - (\delta + \kappa)\tilde{t} + \dots \quad (11c)$$

Obtaining the asymptotic behavior of the reactants for  $t \rightarrow \infty$  is more difficult, since the approximation leading to Equation 5 becomes invalid, and a more formidable approximation of Equation 4 must be treated. This situation arises because of a nonuniformity for  $t \rightarrow \infty$  of the approximation that the second and third terms of the third factor of the denominator of the integrand in Equation 4 are small compared to unity. In particular, the second term is  $O(1)$  as  $t \rightarrow \infty$ . This point will be amplified subsequently.

Still considering our previous case, we examine the three factors which make up this denominator to find that the first has a zero at  $x = 0$ , the second for  $x > 1$  (which is outside the range of integration) and the third, as we will show, has only one zero,  $x_0$  within it. The value  $x_0$  corresponds to the equilibrium concentration of NO attained monotonically from above as  $t \rightarrow \infty$ . If we let  $\kappa = O(\delta)$  as  $\delta \rightarrow 0$ , the root  $x_0$  of the third factor can be shown by iterative substitution to be asymptotically given by:

$$x_0 = \delta[1 + O(\delta \ln \delta)] \text{ as } \delta \rightarrow 0$$

Through justifications given in Appendix B we may approximate Equation 4 as:

$$\tilde{t} = \frac{1}{\rho} \int_B^1 \frac{dx}{x(Dx^{r-1} - 1)(x - x_0)} \quad (12)$$

Further simplification is achieved by defining  $1/F(x) \equiv x(Dx^{r-1} - 1)$ , and subtracting and adding  $F(x_0)$  to the integrand in Equation 13. This gives:

$$\rho\tilde{t} = \int_B^1 \frac{F(x)dx}{x - x_0} \equiv I_1 + I_2 \quad (13a)$$

where

$$I_1(B) = \int_B^1 \frac{F(x_0)dx}{x - x_0} \quad (13b)$$

$$I_2(B) = \int_B^1 \frac{[F(x) - F(x_0)]dx}{x - x_0} \quad (13c)$$

Now the singular behavior as  $B \rightarrow x_0$  is contained entirely in  $I_1$ , since as indicated in Appendix C,  $I_2$  is  $O(1)$  in the indicated limit. Despite the fact  $I_1 = O[\ln(B - x_0)]$  and  $I_2 = O(1)$ , the latter must be retained to obtain the complete leading term of the asymptotic representation of  $B$ . Since



$I_2(B)$  may be approximated by  $I_2(x_0)$  in the sense discussed fully in Appendix C, Equation 13a yields:

$$\rho\bar{\tau} \cong \frac{1}{Dx_0} \ln \left( \frac{1-x_0}{B-x_0} \right) + I_2(x_0) \quad (14)$$

where we have set  $F(x_0) \cong 1/x_0 D$ . Inverting Equation 15, we obtain, for  $t \rightarrow \infty$ ,

$$\frac{(\text{NO})}{(\text{NO})_0} = B = x_0 + e^{-x_0 D [\rho\bar{\tau} - I_2(x_0)]} + \dots \quad (15a)$$

The time constant for the exponential decaying transient in Equation 16a is thus approximately given by  $(\delta^2 D)^{-1}$ . Substitution of Equation 16a into Equation 4 and making appropriate approximations gives:

$$\frac{(\text{NO}_2)}{(\text{NO}_2)_0} = A = (1 + \rho)x_0 \tau \left\{ 1 + \frac{re^{-x_0 D [\rho\bar{\tau} - I_2(x_0)]}}{x_0} + \dots \right\} \quad (15b)$$

$$\frac{(\text{RH})}{(\text{RH})_0} = C = \frac{\delta e^{-x_0 D [\rho\bar{\tau} - I_2(x_0)]}}{x_0^2} + \dots \quad (15c)$$

Thus at long times the NO concentration approaches a very small constant times its initial concentration. This constant,  $x_0$ , is approximately equal to the parameter  $\delta$  which for interesting conditions is always small. The  $\text{NO}_2$  concentration also approaches a constant value, but this one is somewhat larger than  $x_0$ . As expected from analysis of the integral Equation 4, the hydrocarbon approaches zero concentration for long time. This just means that the reactions continue until the hydrocarbons have completely reacted. The parameters,  $\delta$  and  $\tau$ , are inversely proportional to the initial hydrocarbon concentration so the larger this concentration the smaller the final NO concentration, but the longer it takes to reach this concentration.

It is interesting to estimate numerically the time scale  $t_e$  for the NO concentration to approach near steady state. This is accomplished by equating the absolute magnitudes of the two terms on the right hand side of Equation 15a. Thus

$$\frac{\rho}{\tau} t_e = - \frac{\ln x_0}{x_0 D} - I_2(x_0) \quad (16)$$

For Friedlander and Seinfeld's first set of conditions, the value of  $t_e$  can be calculated from the above expression to be 54 min. The concentrations used for this calculation are taken from smog chamber experiments. More realistic values (Hidy et al., 1971) would be  $(\text{NO}_2) = 5$  pphm,  $(\text{NO}) = 8$  pphm, and  $(\text{HC}) = 0.6$  ppm (estimate of reactive component) which are values taken at 8 A.M. in Pasadena, CA. For these values,  $t_e$  gets up to 18 hr.

### Conclusions

By application of analytical techniques, results have been obtained which are difficult if not virtually impossible to obtain by numerical solution. These may be summarized as:

Important dimensionless groupings controlling the kinetics  
Criterion for a peak in the  $\text{NO}_2$  concentration

Value of the peak  $\text{NO}_2$  concentration and the time at which it is obtained

Temporal behavior for small and large times of the species concentrations including their time constants

A characteristic relaxation time for approach to steady state.

As is demonstrated in the appendices, more details may be extracted from this simple model. It may be possible to construct more sophisticated and/or realistic simulations which may be equally analytically tractable.

Since attempts are being made by various groups to model the convective aspects of photochemical smog, results such as those presented above should be of considerable help. In the solution of diffusion models presently suggested, significant mathematical and numerical difficulties arise even when the movement of a single nonreacting pollutant is considered. The analysis of the appropriate coupled systems becomes almost insurmountable for realistic cases and demands intelligent approximations to allow reasonable solutions. Discovery of the crucial time scales, the essential lumped dimensionless groupings such as those given above may serve as important inputs to approximate solutions of convective models.

### Appendix A. Series Solution for Time of Peak $\text{NO}_2$ Concentration

The result for  $\bar{t}_p$  obtained by substituting Equations 9 into 6 is:

$$\bar{t}_p = \nu \sum_{n=1}^{\infty} \frac{1 - (rD)^{n-Q}}{(n-Q) D^n} \quad \text{where } Q^{-1} \equiv 1 - r \quad (A1)$$

Using values of the parameters and initial conditions in Friedlander and Seinfeld, we obtain  $\nu = 0.2$ ,  $D = 1.16$ , and  $Q = 1.25$ . In this case the series converges slowly to  $\bar{t}_p = 3.99$  ( $t = 16$  min) requiring five terms for 10% accuracy and 15 terms for 1% accuracy. We may write

$$\nu^{-1} \bar{t}_p = \sum_{n=1}^{\infty} \frac{D^{-n}}{n-Q} - \frac{1}{(rD)^Q} \sum_{n=1}^{\infty} \frac{r^n}{n-Q} \quad (A2)$$

Each of the series in Equation A2 is expressible as the  $\Phi$  function [a special form of the hypergeometric function (Erdélyi, 1953)] but this does not simplify their evaluation appreciably. Because of small value of  $r$ , the second series converges very rapidly (similar to a geometric series) requiring only two terms for 1% accuracy in the case above. Since  $D$  is near unity, the first series converges very slowly. However, Kummer's Transformation (Knopp, 1948) may be used to accelerate its convergence. This process yields

$$\nu^{-1} \bar{t}_p = -\ln(1 - D^{-1}) + Q \sum_{n=1}^{\infty} \frac{D^{-n}}{n(n-Q)} - \frac{1}{(rD)^Q} \sum_{n=1}^{\infty} \frac{r^n}{n-Q} \quad (A3)$$

The new series in Equation A3 will now yield 10% accuracy for the above case after only two terms and 1% after six terms.

### Appendix B

The difference between the integrand in Equation 4 and the integrand in Equation 12 may be seen in the following identity:

$$\frac{1}{x + \delta(x-1) + \kappa x \ln x} = \frac{1}{(x-x_0)} \left[ 1 - \frac{x_0 + \delta(x-1) + \kappa x \ln x}{x + \delta(x-1) + \kappa x \ln x} \right] \quad (B1)$$

The left hand side is a factor in the integrand of Equation 4 and

the first term on the right is a factor in the integrand of Equation 12. The second term within the brackets on the left hand side of (B1) can be shown to be bounded and monotonic for  $x > 0$ ,  $\delta > 0$ ,  $0 < x_0 \leq x \leq 1$  with its maximum at  $x_0$  given by

$$\Gamma \equiv \frac{\delta + \kappa(1 + \ln x_0)}{1 + \delta + \kappa(1 + \ln x_0)} = O(\delta \ln \delta) \quad (\text{B2})$$

Thus a lower bound to the integral in Equation 5 is:

$$\rho \tilde{I} \cong \int_B^1 \frac{F(x_0)(1 - \Gamma)}{(x - x_0)} dx + (1 - \Gamma)I_2(x_0) \quad (\text{B3})$$

$$= F(x_0)(1 - \Gamma) \ln \left( \frac{1 - x_0}{B - x_0} \right) + (1 - \Gamma)I_2(x_0) \quad (\text{B4})$$

which may be solved for  $B$ , which we call  $B_1$ , to distinguish it from  $B$  given by Equation 15a, thus:

$$B_1 = x_0 + (1 - x_0) \exp \left\{ -\frac{1}{F(x_0)} \left[ \frac{\rho \tilde{I}}{(1 - \Gamma)} - I_2(x_0) \right] \right\} \quad (\text{B5})$$

Defining

$$\Delta B \equiv B - B_1$$

Then

$$\lim_{\tilde{I} \rightarrow \infty} \frac{\Delta B}{B} = 0$$

which means that the difference between Equations 15a and B5 becomes small compared to  $x_0$  for  $\tilde{I} \rightarrow \infty$ . Since Equation 15a is an upper bound, the two bounds converge and 15a can be taken as an approximation to  $B$ .

### Appendix C

We assert that the following Taylor's Series is a representation of  $I_2$  about  $B$ . (We will not attempt to rigorously establish the formal developments here and in what follows. These require lengthy estimates beyond the scope of this analysis)

$$I_2(B) = \sum_{n=0}^{\infty} \frac{I_2^{(n)}(x_0)}{n!} (B - x_0)^n \quad (\text{C1})$$

Combining this with  $I_1(B)$  in Equation 13a and taking the  $n = 0$  term out of the sum, we obtain for  $\tilde{I}$

$$\rho \tilde{I} = (F x_0) \ln \left( \frac{1 - x_0}{B - x_0} \right) + I_2(x_0) + \sum_{n=1}^{\infty} \frac{I_2^{(n)}(x_0)}{n!} (B - x_0)^n \quad (\text{C2})$$

Rearranging and exponentiating yields

$$e^{-\left[ \frac{\rho \tilde{I} - I_2(x_0)}{F(x_0)} \right]} = \frac{B - x_0}{1 - x_0} \exp \left[ -\sum_{n=1}^{\infty} \frac{I_2^{(n)}(x_0)}{n!} (B - x_0)^n \right] \quad (\text{C3})$$

$$\cong (B - x_0)[1 + O(B - x_0)] \quad (\text{C4})$$

or on rearrangement:

$$B \cong x_0 + (1 - x_0)e^{-\frac{\rho \tilde{I} - I_2(x_0)}{F(x_0)}} \quad (\text{C5})$$

An expression for  $I_2(x_0)$  may be obtained by expanding the

integrand as follows. Letting  $q = n(1 - r) - r$ , and expanding  $F(x)$  and  $F(x_0)$  each about 0, we obtain

$$I_2(x_0) = \int_{x_0}^1 \sum_{n=0}^{\infty} D^{-n} \frac{(x^q - x_0^q)}{x - x_0} dx \quad (\text{C6})$$

Assuming the required convergence properties we interchange summation and integration. We introduce the substitution of variables  $u = x/x_0$  in the resulting integrals [which are qualitatively similar to psi and hypergeometric functions (Erdélyi, 1953)]. Expanding the integrands in ascending powers of  $u^{-1}$  using the binomial theorem, convergent series of the  $\Phi$  function type described in Appendix A are obtained. On performing the required final summation, we obtain under the additional assumption of small  $r$ :

$$I_2(x_0) \cong \frac{1}{D x_0^r} \left[ \ln x_0 - \gamma + \frac{1}{r} F \left( 1, \frac{-r}{1-r}; \frac{1-2r}{1-r}; \frac{x_0^{1-r}}{D} \right) - \psi(1-r) \right] - \frac{1}{rD} F \left( 1, \frac{-r}{1-r}; \frac{1-2r}{1-r}; \frac{1}{D} \right) \quad (\text{C7})$$

where  $\gamma$  is Euler's constant = 0.57721,  $F(a;b;c;z)$  is the hypergeometric function, and  $\psi$  is the psi function (logarithmic derivative of the gamma function). For numerical purposes, the third term above may be evaluated by series expansion in  $z$  (the first term being overwhelmingly the most important), but in the fifth, slow convergence for the numerical case considered obtains due to the near unity value of  $D$ . This reflects proximity to a logarithmic singularity occurring on the unit circle. For this purpose, either a special expansion above unity (see Abramowitz and Stegun, 1964) or an expansion for  $r \rightarrow 0$  can be used. For the numerical parameters used earlier in this paper,  $I_2(x_0)$  was evaluated numerically, yielding 8.134. The above expression agrees within 1% with this value.

### Acknowledgment

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### Nomenclature

- $A \equiv (\text{NO}_2)/(\text{NO}_2)_0$
- $B \equiv (\text{NO})/(\text{NO})_0$
- $C \equiv (\text{RH})/(\text{RH})_0$
- $D \equiv (1 + \rho)/\rho$
- $d \equiv D^{1/4}$
- $n \equiv$  integer index of a power series
- $O \equiv$  the order of (see Erdélyi, 1956)
- $p \equiv$  subscript denoting the value of the variable when  $(\text{NO}_2)$  reaches its peak value
- $Q \equiv 1/(1 - r)$
- $q \equiv$  an arbitrary real number representing a typical value of a power in a series expansion (see Equation C7)
- $r \equiv \lambda/\alpha$
- $t \equiv$  time, min
- $\tilde{I} \equiv \frac{\rho \tilde{I}}{r}$ , dimensionless time
- $x \equiv$  dummy variable of integration
- $x_0 \equiv$  zero of  $(1 + \delta)x - \delta + \kappa \ln x$ ; this is the value of  $B$  for which  $C = 0$

### GREEK LETTERS

- $\delta \equiv \mu/[\alpha(\text{NO})_0(\text{RH})_0]$

$$\begin{aligned} \zeta &\equiv k_7(\text{NO})_2 - (\epsilon - 1)k_6(\text{NO}) \\ \kappa &\equiv \theta/[\alpha(\text{RH})_0] \\ \nu &\equiv (\text{NO}_2)_0/(\text{NO})_0 \\ \rho &\equiv Q/\nu \\ \tau &\equiv 1/[\alpha(\text{NO}_2)_0(\text{RH})_0] \end{aligned}$$

Notation from Friedlander and Seinfeld (1969)

$$\begin{aligned} \alpha &\equiv \gamma k_6 k_4' \\ \beta &\equiv k_1/k_3 \\ \gamma &\equiv k_1/k_2 \\ \lambda &\equiv \gamma k_7 k_4' \\ \mu &\equiv \beta k_5 \\ \theta &\equiv \gamma k_4 \\ \epsilon &\equiv \text{a branching factor accounting for possible production of more } R\cdot \text{ than consumed in Reaction 6 below} \\ k_1 &\equiv \text{rate constant for } \text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}, \text{ includes light intensity} \\ k_2 &\equiv \text{rate constant for } \text{O} + \text{O}_2 \xrightarrow{M} \text{O}_3, \text{ includes third body } M \text{ and } \text{O}_2 \text{ concentration} \\ k_3 &\equiv \text{rate constant for } \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \\ k_4 &\equiv \text{rate constant for } \text{RH} + \text{O} \rightarrow R\cdot + \text{Products, where RH and } R\cdot \text{ are generalized hydrocarbon and free radical, respectively} \end{aligned}$$

$$\begin{aligned} k_5 &\equiv \text{rate constant for } \text{RH} + \text{O}_3 \rightarrow \text{products (including } R\cdot) \\ k_6 &\equiv \text{rate constant for } \text{NO} + R\cdot \rightarrow \text{NO}_2 + R\cdot \\ k_7 &\equiv \text{rate constant for } \text{NO}_2 + R\cdot \rightarrow \text{products (including PAN)} \\ k_4' &\equiv k_4/\zeta \end{aligned}$$

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## COMMUNICATIONS

### Singlet O<sub>2</sub> Production from Photoexcited NO<sub>2</sub>

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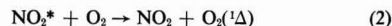
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■ Mixtures of NO<sub>2</sub> and O<sub>2</sub> were irradiated with visible light. ( $\lambda > 4000\text{\AA}$ ). Electronically excited NO<sub>2</sub> was produced which transferred energy collisionally to O<sub>2</sub> to produce O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>). The population of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) in the reaction cell was determined by monitoring its phosphorescent emission at 1.27 μ with an RCA 7102 photomultiplier used in a photon-counting mode. From the experimentally determined rate of production and destruction of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>), the probability that a quenching collision of NO<sub>2</sub>\* with O<sub>2</sub> will produce O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) is found to be  $\alpha = 0.01 \pm 0.002$ . This mechanism is capable of producing a steady-state O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) concentration in the atmosphere of 10<sup>7</sup>-10<sup>8</sup> cm<sup>-3</sup>.

The possibility that singlet molecular oxygen might play a noticeable role in the photochemical smog cycle was pointed out by Pitts (1969). Herron and Huie (1969) found the relative reactivities of single molecular oxygen, oxygen atom, and ozone to be 10<sup>-2</sup>:1:1 at best and concluded that known mechanisms for producing metastable O<sub>2</sub> molecules were not sufficiently effective to make these species important in the smog cycle. Subsequent work indicates the reactivity ratio may be more like 10<sup>-4</sup>:1:1 (Johnston et al., 1971). About the same time, Kummeler and Bortner (1969), Steer et al. (1969b), and Snelling (1968) showed that benzaldehyde, benzene, naphthalene, and naphthalene derivatives

could absorb light and transfer this energy to O<sub>2</sub> to produce excited oxygen molecules. Still, these mechanisms seem too inefficient to be important for smog formation because of the low ambient concentrations of the photosensitizing species and their small extinction coefficients in the visible or near-uv spectral regions.

We have investigated another possible mechanism for generating singlet molecular oxygen, the production of O<sub>2</sub>(<sup>1</sup>Δ) by the NO<sub>2</sub>-photosensitized process



This process was studied by irradiation of NO<sub>2</sub>-O<sub>2</sub> mixtures with a chopped, carefully filtered beam of visible light. Wavelengths below 4000Å were excluded to avoid photodissociation of the NO<sub>2</sub> (Douglas and Huber, 1965; Schuck et al., 1966; Cvetanovic, 1964). Direct measurement of the 1.27-μ emission from the process O<sub>2</sub>(<sup>1</sup>Δ) → O<sub>2</sub>(<sup>3</sup>Σ) + hν was used to monitor the energy transfer. Emission was observed through two Corning No. 7-56 filters with an RCA 7102 photomultiplier operated as a photon counter. The emission was confirmed as originating only at 1.27 μ by scanning the line with a temperature-tuned, narrow band interference filter (Razdow Optical Instruments, 1.2728 μ peak transmission at 20°C). The photomultiplier tube was calibrated against a blackbody source with various filter combinations. Under our operating conditions, the quantum efficiency of the tube at 1.27 μ is 1.5 × 10<sup>-7</sup>. The observed signal was about 4 counts/sec. Modulation at 30 Hz was as follows: The sample was irradiated during the first 1/4 cycle; after 1/8-cycle delay, the photomultiplier

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was gated on for  $1/2$  cycle, the final  $1/8$  cycle was dead time.

The pressure dependence of both the near-ir and visible  $\text{NO}_2$  emission gave Stern-Volmer plots which yielded values for  $\text{NO}_2$  quenching by  $\text{N}_2$  and by  $\text{O}_2$  in essential agreement with those in the literature (Meyers et al., 1966; Schwartz, 1968).

In a typical experiment,  $p(\text{NO}_2) \cong 0.48$  torr,  $p(\text{O}_2) \cong 3.0$  torr, and the system absorbs approximately  $5.4 \times 10^{15}$  photons/sec, all in the wavelength range 4000–5000Å. From geometric factors and the observed rate of emission by  $\text{O}_2(^1\Delta)$ , we estimated a total  $\text{O}_2(^1\Delta)$  production rate of  $4.1 \times 10^{13}$ /sec. These diffuse uniformly throughout a cell of  $860 \text{ cm}^3$ , in the irradiation interval. Deactivation of excited  $\text{O}_2$  molecules is due to wall collisions, to collisions with  $\text{NO}_2$ , to collisions with  $\text{O}_2$  and, in very small part, to radiation. The pseudo first-order rate coefficients for the first three processes are  $0.10 \text{ sec}^{-1}$  (in our system),  $0.08 \text{ sec}^{-1}$ , and  $0.21 \text{ sec}^{-1}$ , respectively (Becker et al., 1971; Steer et al., 1969a); the radiative rate is  $2.58 \times 10^{-4} \text{ sec}^{-1}$ . The system is in a steady state with respect to  $\text{O}_2(^1\Delta)$ , with an effective total first-order decay constant of  $0.39 \text{ sec}^{-1}$ .

From the known quenching constants (Meyers et al., 1966; Schwartz, 1968) for  $\text{NO}_2^*$  by  $\text{NO}_2$  ( $7.1 \times 10^{-11} \text{ cm}^3/\text{mol-sec}$ ), the measured concentrations of  $\text{NO}_2$  and  $\text{O}_2$ , and the knowledge that  $\text{NO}_2$  fluorescence is completely quenched, we determine that fraction of photons absorbed which go one way or another to  $\text{O}_2$ . From the experimentally determined rate of production (and destruction) of  $\text{O}_2(^1\Delta)$ , we thus determine the probability,  $\alpha$ , that a quenching collision of  $\text{NO}_2^*$  with  $\text{O}_2$  will produce  $\text{O}_2(^1\Delta)$ :

$$\alpha = 0.01 \pm 0.002 \quad (3)$$

The uncertainty is due largely to uncertainties in collection efficiency from molecules away from the optic axis of the photomultiplier. In other words, about 1% of the collisions of  $\text{NO}_2^*$  with  $\text{O}_2$  yield a metastable  $\text{O}_2(^1\Delta)$ .

The possible significance of this observation for the problem of smog appears when we estimate the ambient concentration of  $\text{O}_2(^1\Delta)$  from the  $\text{NO}_2$ -activated process alone. The rate constant for quenching of  $\text{NO}_2^*$  by  $\text{N}_2$  is  $3.1 \times 10^{-11} \text{ cm}^3/\text{mol-sec}$ , slightly less than that for quenching by  $\text{O}_2$ . From these two coefficients, we infer that about 21.5% of the  $\text{NO}_2^*$  in the atmosphere lose their energy to  $\text{O}_2$ , and thus about 0.215% of the excited  $\text{NO}_2^*$  molecules generate  $\text{O}_2(^1\Delta)$ . ( $\text{NO}_2$  fluorescence is, of course, completely quenched in the atmosphere.) The rate of production of  $\text{NO}_2^*$  by light in the 4000–5000Å region, when the  $\text{NO}_2$  concentration is 0.035 ppm and the photon flux in the 4000–5000Å interval is  $5 \times 10^{16}/\text{cm}^2\text{-sec}$ —corresponding to the sun  $40^\circ$  from the zenith, on a clear day—is about  $2.3 \times 10^{10}/\text{cm}^2\text{-sec}$ . Hence the rate of production of  $\text{O}_2(^1\Delta)$  under these conditions is about  $4.35 \times 10^7/\text{cm}^2\text{-sec}$ . The  $\text{O}_2(^1\Delta)$  is in a steady-state condition, with most of its quenching accomplished by  $\text{O}_2$ ; the rate coefficient for this process is  $2.2 \times 10^{-18} \text{ cm}^3/\text{mol-sec}$ . Hence the pseudo first-order rate coefficient for deactivation of  $\text{O}_2(^1\Delta)$  is  $12 \text{ sec}^{-1}$ , and the steady-state concentration of  $\text{O}_2(^1\Delta)$  under the conditions just described is  $3.6 \times 10^6/\text{cm}^3$ .

More generally, we can express the steady-state concentration of  $\text{O}_2(^1\Delta)$ , in molecules/ $\text{cm}^3$ , in terms of the photon flux  $\phi$  (as  $10^{16}$  photons/ $\text{cm}^2\text{-sec}$ ) and the  $\text{NO}_2$  concentration (in the common units of ppm) as

$$[\text{O}_2(^1\Delta)] = 2 \times 10^7(\text{NO}_2, \text{ppm})\phi \quad (4)$$

Under conditions of intense sunlight and moderately high concentrations of  $\text{NO}_2$ , the steady-state concentration of

$\text{O}_2(^1\Delta)$  easily exceeds  $10^7 \text{ cm}^{-3}$  and may reach  $10^8 \text{ cm}^{-3}$  as a result of the  $\text{NO}_2$ -activated mechanism alone. The concentration of O atoms is probably seldom greater than  $5 \times 10^5 \text{ cm}^{-3}$  (Berry and Lehman, 1971) and may be up to an order of magnitude lower than this during earlier stages of the smog cycle (Johnston et al., 1971). It thus appears the  $\text{NO}_2$ -activated mechanism by itself is capable of producing sufficient  $\text{O}_2(^1\Delta)$  to make singlet molecular oxygen a contributor to smog formation despite the  $10^2$ – $10^4$ -fold lower activity of the molecular species.

Early work on the photooxidation of hydrocarbons in the presence of  $\text{NO}_2$  (Bufalini and Altshuler, 1967) indicated that the rate of hydrocarbon oxidation could be explained solely on the basis of O-atom oxidation. However, it should be noted that these experiments were conducted using uv light which photodissociates  $\text{NO}_2$  to  $\text{NO} + \text{O}$  quite efficiently and produces very little  $\text{NO}_2^*$ . Thus these early experiments were under conditions where  $[\text{O}_2(^1\Delta)] \ll 10^4$  (O) and therefore have no bearing either positive or negative on the role of  $\text{O}_2(^1\Delta)$  in the atmospheric oxidation of hydrocarbons.

In addition to the high  $\text{NO}_2$  concentration experiments mentioned above, we have conducted experiments with the  $\text{NO}_2$  concentration as low as 500 ppm and find the mechanism for  $\text{O}_2(^1\Delta)$  formation remains operative. This strongly indicates that the energy transfer is truly an elementary molecular process and thus our extension to the atmosphere is valid.

After this work was submitted for publication, we learned that very similar conclusions have been reached by Jones and Bayes (1971) based on a very different detection method.

A more detailed discussion, including a study of the  $^1\Sigma$  state, is in preparation.

#### Acknowledgment

We would like to thank Peter A. Lehman for his stimulating comments.

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# Sunlight Photochemistry of Ferric Nitrilotriacetate Complexes

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■ Photochemical degradation under natural water conditions of the acidic solution monomeric and the basic solution monomeric and dimeric complexes formed between Fe<sup>3+</sup> and nitrilotriacetic acid (NTA) is described. The degradation products are CO<sub>2</sub>, CH<sub>2</sub>O, and iminodiacetic acid (IDA). The efficiency declines somewhat with increasing pH but quantum yields above approximately 0.01 may be expected in all natural waters. The evidence for such photodegradation serving as a mechanism to limit accumulation of NTA in natural waters is discussed.

The fate of aminopolycarboxylate compounds (which are all potential detergent builders and are important components of industrial wastes) in natural waters must be the fate of their metal complexes since complex formation constants (Ringbom, 1963) with all common metal ions are so large. The largest formation constants for nitrilotriacetic acid (NTA) are those for formation of ferric complexes.

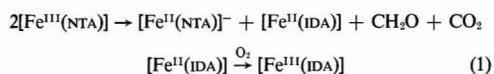
Equilibrium calculations on a model of Lake Ontario (Childs, 1971) conclude that the fraction of NTA bound in ferric complexes varies between 6 and 36% of the total NTA in the water for total NTA concentrations from 10<sup>-7</sup> to 10<sup>-5</sup>M. These calculations probably underestimate the ferric NTA species because they limit Fe to that found in the absence of NTA and intentionally ignore solubilization of ferric oxide by NTA.

We have undertaken a study of the photochemistry of ferric NTA complexes using irradiation characteristic of sunlight. In initial experiments, solutions were prepared containing 0.010M Fe<sup>3+</sup> and 0.010M NTA (to provide convenient concentrations of ferric NTA species). pH values were adjusted from 4 to 8 to cover the freshwater range indicated by Mason (1952) and to ensure examination of all of the hydrolytic forms of ferric NTA (Childs, 1971; Gustafson and Martel, 1963). The solutions were enclosed in borosilicate glass flasks and irradiated outdoors in varying light conditions. In all experiments, precipitation of iron was complete in less than 14 days, indicating extensive degradation of the solubilizing agent, NTA. No reaction was observed in dark controls.

Examination of the stoichiometry of the photodegradation was developed following the hint provided by the known photodecarboxylation of carboxylic acids coordinated to Fe(III) (Balzani and Carassiti, 1970), and the observation of Hall and Lambert (1968) that ethylenediaminetetraacetate (EDTA) complexes of Fe(III) release CO<sub>2</sub> on irradiation. Solutions irradiated in a Rayonet photoreactor equipped with 3500Å fluorescence-coated mercury lamps to greater than 10% loss of NTA were examined for products. Aldehydes were detected by Schiff's test, phenylenediamine-H<sub>2</sub>O<sub>2</sub> reagent, and finally a carbazole test. Taken together, these

indicate formaldehyde (Feigl, 1954). Solid derivatives of the aldehyde could be isolated. A 2,4-dinitrophenylhydrazone melting at 163.5–165.0°C and a *p*-nitrophenylhydrazone melting at 155–165°C confirm the identification of formaldehyde. An amine product was sought. A ninhydrin test was positive indicating an  $\alpha$  or  $\beta$  amino acid or a primary or secondary amine. This requires that NTA has lost at least one —CH<sub>2</sub>COOH claw. By acidification of the solution, a white solid could be isolated which formed amine derivatives with phenyl urea and *p*-toluenesulfonyl chloride. (Melting points were ca. 195° and 65–65.5°C, respectively.) These derivatives correspond to those prepared from an authentic sample of iminodiacetic acid (IDA) (mp, 195° and 65–67°C). A quantitative determination of the IDA yield was achieved using ninhydrin and the procedure of Moore and Stein (1948). A solution which had decreased in NTA concentration by 0.0015M (according to the titrations described below) was found to have an amine concentration of 0.0016M. More than 90% of the NTA nitrogen appears in an amine product (presumably all IDA).

Equation 1 is proposed to describe the photodecomposition of NTA. [In the equation, the low pH form of Fe(NTA) is indicated. Hydrolyzed species appear at higher pH.]



The second step occurs in the presence of air and interferes with attempts to determine stoichiometry of the first step with respect to iron. Irradiations were carried out to confirm stoichiometry with respect to iron. Solutions were deoxygenated by bubbling through nitrogen for 20 min then sealing the flasks with serum caps. After suitable times of irradiation, samples were withdrawn with a syringe and analyzed for Fe<sup>2+</sup> by the *o*-phenanthroline method (Hatchard and Parker, 1956) and formaldehyde by spectrophotometric determination of the 2,4-dinitrophenylhydrazone derivative dissolved in acetone. The ratio of Fe<sup>2+</sup>/CH<sub>2</sub>O is close to 2 after short irradiation times in the Rayonet reactor (1.93 after 10 min, 2.20 after 20 min) but rises at longer times. (The puzzle was resolved by observing a secondary reaction, an acidified solution of formaldehyde and Fe<sup>3+</sup> irradiated at 3500Å showed reduction of Fe<sup>3+</sup> and oxidation of CH<sub>2</sub>O.) The stoichiometry of Equation 1 is confirmed by study of the Fe<sup>2+</sup>/CH<sub>2</sub>O product ratio.

There remains the problem of the efficiency of the photodegradation of NTA. We believe that the photochemical reaction originates from a charge transfer excited state of the complex. Efficiency is not a simple matter over the range of pH found in natural waters because there is not a single

Table I. Values of the Quantum Yield-Related Function Y (Defined in the Text) as a Function of pH

pH	4.25	4.73	6.10	7.00	7.65
Y	0.078	0.089	0.047	0.039	0.018

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ferric complex. At higher pH, Fe(NTA) forms an oxo-bridged dimer (Gustafson and Martel, 1963) so that efficiency may be expected to vary with pH. The efficiency was measured under irradiation with a GE mercury lamp, TP 109, which has strong emission at 3660, 4100, 4400, 5750, and 6500Å. The measure of reaction was the amount of NTA decomposed. This was determined by titration of NTA remaining after a period of irradiation by one of two methods. In the first, activity of iron in the solution was minimized by adjusting the pH to 9.4 and addition of an equal volume of 0.01M sodium acetate after which NTA could be titrated with Cu(II) to a murexide end point. In the second, the Bi(III) complex of NTA was formed after acidification of the solution to a pH of 1.00 and determined spectrophotometrically at 2430Å (Karadakov and Vankava, 1970).

The best measure of efficiency is quantum yield but that is difficult to determine in the case of irradiation with a wide wavelength range source. As an approximation, we compare yields to the yields for the standard chemical actinometer system, ferrioxalate (Hatchard and Parker, 1956) and define a function related to quantum yield,  $Y$ , equal to the ratio of moles NTA decomposed to the moles of Fe(II) produced from ferrioxalate multiplied by the quantum yield for reduction of ferrioxalate at 3660Å. Values appear in Table I. The observed decline in  $Y$  with increasing pH may be associated with facile relaxation of the charge transfer states of the Fe(NTA) system in the dimer form where the spin forbidden character of radiationless transitions to the ligand field states is relaxed. We intend to discuss this issue elsewhere.

The photochemical mode of NTA degradation should be of significance in limiting the accumulation of NTA (and most

probably related aminopolycarboxylates) in natural waters if it can be shown that the actinic light is available. Whether photosynthesis can occur in natural waters is essentially the same question since the actinic wavelengths are very close. The euphotic zone may vary from a depth of less than a meter in an unusually turbid river to over 100 meters in clear ocean water. Duntley's review of near uv penetration (Duntley, 1963) suggests that the reaction described here would be important to depths of at least 10 meters in typical situations.

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## CORRESPONDENCE

### Uranium Concentrations in Surface Air

SIR: The article "Uranium Concentrations in Surface Air at Rural and Urban Localities within New York State" (ES&T, August 1971, p 700) states on p 703: "These levels are much less than the 90 and 300 ng U/m<sup>3</sup> levels found near gaseous diffusion plants at Paducah, KY, and Piketon, OH, respectively." These values are compared with values found in various parts of New York State ranging from 0.1 to 1.47 ng U/m<sup>3</sup>.

The statement would lead a reader to conclude that the diffusion plants emit large mass quantities of uranium to the atmosphere; and, indeed, such a conclusion would be reached if one assumed that the radioactivity levels at the Piketon plant were 5% of the radioactivity concentration standards and that the source was normal assay uranium. However, neither assumption is valid. The official reports from the Piketon plant state that the average radioactivity level is "less than 5%" of the applicable standards. A more significant error lies in the assumption that uranium discharged from the Piketon plant is of normal assay; and it is obvious that this assumption was made by the authors. The article reports all measurements in mass concentration units (ng U/m<sup>3</sup>), whereas

all the data reported by the Piketon plant are given in radioactivity concentration units. To convert from one set of units to the other set, the uranium isotope assay must be known.

If one assumes that the uranium is of normal assay and that the radioactivity level is 5% of the applicable standard, he will reach the same conclusion reached by the authors—i.e., 300 ng U/m<sup>3</sup>. However, the Piketon plant is an enrichment plant, and the concentrations of radioactive isotopes of uranium, other than U-238—i.e., the enrichment, may be as great as 94%. The specific activity of the enriched uranium may be 200 times as great as that of normal assay uranium. Obviously, then, the calculated mass concentrations, 300 ng U/m<sup>3</sup>, is incorrect, perhaps by a factor of 200—two orders of magnitude.

I feel that this should be pointed out to your readers to correct any possible misinterpretation.

Ben Kalmon

Industrial Hygiene & Health Physics  
Goodyear Atomic Corp.  
Piketon, OH 45661

SIR: The authors read with interest the comments of Mr. Kalmon and appreciate the opportunity to discuss the issues he has raised. Mr. Kalmon's remarks pertaining to the conversion of radioactivity units to mass units is well-taken and recognized by the authors. Admittedly, a direct conversion requires knowledge of the isotopic composition of the sample. Although the authors were certainly receptive to any information which would clearly define the uranium levels existing near such facilities, precise isotopic data was not available. However, with respect to the uranium concentrations cited for the Paducah, KY and Piketon, OH gaseous diffusion plants, the values listed were included primarily to provide a comparison (order of magnitude) with levels found in the New York State survey, and were in no way an attempt to single out specific uranium sources or that of the nuclear industry in general.

In regard to the asserted incorrect assumptions made by the authors pertaining to the uranium assay of samples taken near the above sites, the Piketon plant concentration of 300 ng U/m<sup>3</sup> cited is based on an average alpha activity of 0.1 pCi/m<sup>3</sup> listed on p 216 of the April 1970 issue (Vol. 11, No. 4) of *Radiological Health Data and Reports* put out by NRC. This data, references to have been provided by Mr. Kalmon himself, follows a short paragraph which specifically states, "Natural uranium and thorium-234 are the most likely radionuclides to be released to the environment by the Portsmouth area gaseous diffusion plant." Based on this clearly stated information, a direct conversion was made to arrive at the 300 ng U/m<sup>3</sup> figure. We might add that there was no attempt on the author's part to exaggerate the levels of uranium near these sites, for if such were the case the 2.4 pCi/m<sup>3</sup> level (~7200 ng/m<sup>3</sup>) recorded and listed in the July-December 1970 report could have been cited.

With respect to the 90 ng U/m<sup>3</sup> level cited for the Paducah, KY plant, this figure was calculated from Table 6, p 214 of the above report which listed a mean uranium alpha radioactivity of 0.03 pCi/m<sup>3</sup>. The conversion to mass units in this case was based on superscript *b* of this table which states that the alpha radioactivity concentrations listed were calculated using the NBS Handbook 69 definition that "a microcurie of recently extracted normal uranium corresponds to 7.57 ×

10<sup>4</sup> alpha dis/sec." This information indicated that the uranium concentrations found in the outdoor air samples had an isotopic assay representative of natural uranium.

Granted that gaseous diffusion plants enrich uranium isotopes having high specific activities, it follows that such plants, whose feed is primarily natural uranium must likewise show a material balance whereby the integrated loss of uranium to the environment would have an assay representative of the feed, unless it is suggested by Mr. Kalmon that only the highly enriched material is preferentially lost. It would seem more likely that special precautions are taken to prevent loss of this valuable portion of the process, with less attention afforded the feed and depleted material streams. The authors do not pretend to know the intricate operations of a gaseous diffusion plant. However, it is common knowledge that the total rate of flow of low enriched material in the plant is on the order of 10<sup>7</sup> times larger than the final product (~94% U<sup>235</sup>) flow rate. The inference, therefore, made by Kalmon that because such plants produce enriched uranium, the alpha activity recorded in the local environs would be due primarily to highly enriched uranium, is very misleading. The radioactivity from the overwhelming quantities of U<sup>238</sup> present in such plant operations would predominate over the combined activities of the other uranium isotopes present in any significant amounts.

Consequently, the authors contend that the figures of 300 and 90 ng U/m<sup>3</sup> cited, although not analytically precise, are representative of levels near such plants, and are definitely not two orders of magnitude high, as suggested by Kalmon. If there is data to the contrary, it should be made available. The authors suspect that such information does not exist, and would like to emphasize that it was one of the objectives of the subject uranium survey to stress the need to make isotopic assays of environmental samples to prevent misinterpretation of data. The determination of gross alpha and beta activity can no longer be considered sufficient in describing the effluents from nuclear industrial sources.

Willard G. Myers

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# industry trends

**General Motors'** Saginaw Steering Gear division has put a closed-loop system into operation for recycling and reusing more than a million gallons of industrial oils annually. The system is on line at GM's Chevrolet manufacturing complex in Saginaw, MI.

**Republic Steel** will begin work on five new air pollution control projects at its Cleveland district steel plant. Republic will spend more than \$3 million to upgrade control facilities for basic oxygen furnaces and open hearth furnaces and the coking plant. Work will be complete by the middle of 1973.

**Laboratoria Ostrea, Inc.**, is a new company formed to provide aquatic environmental services. The company, located in Jupiter, FL, will concentrate on ecological impact studies, environmental education programs, and maricultural services.

**Research-Cottrell** has received an order to install two electrostatic precipitator complexes to control catalyst emissions from fluid catalytic cracking at Gulf Oil Co.'s Port Arthur, TX, refinery. Each complex will contain three precipitator units—two for constant use and one for standby use.

**Water Works Supply & Mfg. Co.**, a wholly owned subsidiary of Certaineed Products Corp., has acquired Vincent Supply Co., a Sacramento, CA, supply house for the water works industry.

**The Ralph M. Parsons Co.** (Los Angeles, CA) has received a contract from the Municipal Sewerage Authority of Guayaquil, Ecuador, to provide engineering and construction supervision for a new \$12 million sewerage system for Guayaquil.

**Combustion Engineering** has received a \$58 million contract from Georgia Power Co., a subsidiary of the Southern Co., for two 880-MW proprietary Combined Circulation steam generators. The units are destined for a new power generation station on the Chattahoochee River near Franklin, GA, about 30 miles southwest of Atlanta.

**Babcock and Wilcox** will provide a two-drum Stirling power boiler for the Pepeecko, HA, sugar cane mill of the

Hilo Coast Processing Co. The \$1.5 million boiler will burn bagasse and generate steam to be used by Hilo Electric Light Co., to produce electricity.

**Ecological Research and Development Corp.** (ECORD, Los Angeles, CA) has been formed to develop and market ecologically related products for industry. First product is a device which rids water systems of corrosion.

**Jacobs Engineering** (Pasadena, CA) and Gulf Degremont, Inc., will jointly build a \$6 million waste water treatment facility for Gulf Oil Co.'s Philadelphia, PA, refinery. The system, to be completed in late 1972 will minimize harmful effects of effluent discharged to the Schuylkill River and the Delaware River Basin.

**Simpson Lee Paper Co.** (San Francisco, CA) will shut down its Everett, WA, pulp and paper mill because operating costs, including necessary investments in environmental control make the operation uneconomical.

**Systems Associates** (Long Beach, CA) and Brown and Caldwell (San Francisco, CA) have been awarded a \$700,000 contract to study water resources for more than 650 miles of coastline stretching from Ventura County to north of Eureka, by the California Water Resources Control Board.

**Bionomic Control Corp.** (Rockville, MD) has received a contract from the Municipal Technology Division of EPA to build a new central sanitary facility for the village of Emmonak in Alaska. The unit will provide community bathing, sauna, laundry, and toilet facilities, and perform all sewage and waste disposal operations for a village of 440 people.

**Scott Research Laboratories** (Plumsteadville, PA) has completed a two-year study of air pollution emissions for the National Coil Coaters Association.

**Bethlehem Mines Corp.** has begun construction of two separate baghouse facilities to reduce air pollution from the Company's Millard lime quarry in Annville, PA. Cost is estimated to be about \$2.4 million.



# new products



## Testing service

Comprehensive environmental testing service for nuclear power system component manufacturers will use nuclear environmental test apparatus developed by company for testing air cleaning components. Mine Safety Appliances, Inc. **61**

## Samplers

Isolok sampler series is specifically adapted for collecting composite samples of viscous or highly abrasive slurries. Accommodates solid particles up to  $\frac{5}{16}$ -in. diameter. Bristol Engineering Co. **62**

## NO<sub>x</sub> monitor

Instrument is designed to measure oxides of nitrogen, specifically nitrogen dioxide and nitric oxide continuously. Uses second derivative spectroscopy to measure components. Spectrometrics of Florida, Inc. **63**

## Venturi scrubber

New Venturi scrubber boasts high-efficiency, large-volume scrubbing for removal of particulate matter and gaseous pollutants from power plant stacks, industrial incinerators, and power boilers. Air Pollution Industries, Inc. **64**

## Bag collector

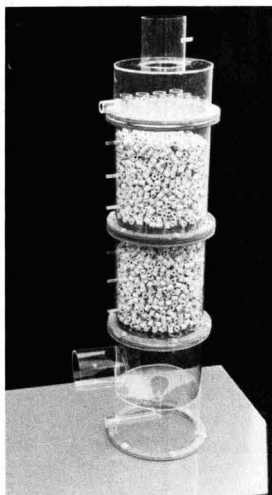
Sky-Kleen H Pulsamatic High Ratio Collector provides exceptional dust collection efficiency with significant savings in both space and cost. Air-to-cloth ratios range from 6:1 to 10:1 and higher, depending on application, grain-loading, and other factors. Johnson March Corp. **65**

## Cadmium detection

Kit provides quick, easy, and inexpensive color spot test to detect cadmium with sensitivity of approximately 0.2 ppm. Each kit performs about 50 tests. Koslow Scientific Co. **66**

## Calibrator

Source emission sample conditioner and calibration system is mounted in single enclosure for either fixed or mobile installation. Provision is made for front panel control and introduction of up to three calibration gases to monitor. Theta Sensors, Inc. **67**



## Models

Simulate air pollution control devices for teaching purposes. Models include reverse flow cyclone, venturi wet scrubber, impingement plate scrubber, bag filter, packed tower, and spray tower. Lace Engineering **68**

## Surveillance monitors

Battery-powered Series 3000 analyzers/recorders operate unattended for 30-day periods. Continuously record pH, DO, conductivity (TDS) or ORP. Delta Scientific Corp. **69**

## Pocket filter

Pocket filter boasts unique cleaning system that extends fabric life by several years. Cleans from the clean air side with alternating reversible purge airflow. Peabody Engineering Corp. **70**

## IR cell

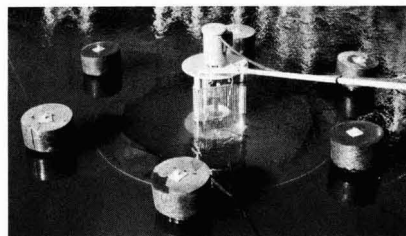
Teflon-lined, beam conforming gas cell has exceptionally high path length-to-volume ratio—4.3 to 1.0 cc as compared with 0.5 to 0.7 cc for conventional tubular cells. Fifty- or 100-mm path lengths available with choice of 10 window materials. Barnes Engineering Co. **71**

## Dryer

Unit reduces water vapor concentration in sample streams being monitored for CO, SO<sub>2</sub>, and NO<sub>x</sub> without changing gas concentrations. Permits greater sensitivity for all optical analyzers used to monitor these gases. Perma-Pure Products, Inc. **72**

## Conductivity meters

Battery- or line-powered meters give high accuracy over wide range of conductivity measurements from high-purity water to concentrated strong acid solutions. Range is expandable in five decades. Probe is tungsten electrode dip cell which includes automatic temperature compensation from 0–100°C. Hach Chemical Co. **73**



## Oil skimmer

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# new literature

**Wastewater concentrator.** Bulletin describes compact, portable waste water concentrator for low-cost primary and tertiary treatment. SWECO, Inc. 91

**Noise control.** Bulletin graphically details causes and effects of industrial noise and methods of control. Industrial Acoustics Co., Inc. 92

**Catalog.** 44-page catalog lists instruments and apparatus for air sampling, monitoring, and analysis. Catalog contains illustrations and listings for more than 400 items. Curtin Scientific Co. 93

**Compost culture.** Literature describes product which aids in rapid decomposition of large quantities of waste vegetation. Judd Ringer Corp. 94

**Smoke monitor.** Brochure describes photoelectric instrument for measuring particulate matter in stack gases. Baldwin Electronics, Inc. 95

**Wildlife enhancement.** Leaflet describes company's services in design of programs for industry which enhance fish and wildlife resources in industrial areas. Aquatic Control 96

**Hot-mix pollution control.** Bulletin describes systems available for controlling air pollution from hot-mix plants. American Air Filter Co., Inc. 97

**Filter racks and chests.** New literature package describes line of air filter racks and filter chests for large-volume air or gas purification. Barneby-Cheney 98

**Analytical services.** Bulletin No. 300 tells story of company's custom analytical services for water supplies, municipal and industrial wastes, fuels, and combustibles. International Hydrionics Corp. 99

**Pond liners.** Handbook and installation guide gives details about asphalt-sealed membrane for pond liners and erosion control. Phillips Petroleum Co. 100

**Planning and control.** Full-color brochure describes resources of company in systems engineering/computer technology approach to environmental problems. Computer Sciences Corp. 101

**Meteorological instruments.** Brochure describes air pollution and meteorological instruments. Includes data sheets on some NOAA-specified systems. Climatronics Corp. 102

**Health services.** Company is offering booklet entitled "How Dow Environmental Health Services Can Help Safeguard You, Your Employees, and the Environment." Dow Chemical Co. 103

**Process control analyzer.** Illustrated bulletin describes complete chemical

analysis system that performs 58 different water and waste tests. Delta Scientific Corp. 104

**Bypass rotameters.** Catalog tells of series of bypass rotameters for economical measurement of large fluid flow rates. Brooks Instrument Div. 105

**Emission measurement systems.** Bulletin describes complete measurement systems for gasoline, diesel, and gas turbine emissions. Beckman Instruments, Inc. 106

**Dust control.** Pocket reference gives data on dust control with Coherex emulsion of petroleum oils and resins. Witco Chemical 107

**Ion Exchange.** Technical report details four years operating experience with company's C.I. Continuous Counter-current Ion Exchange Process. Discusses mixed-bed, two-bed, zeolyte-softening, and sodium-hydrogen blend systems. Graver Water Conditioning Co. 108

**Data system.** Bulletin tells of new data system developed for Du Pont 21-490 series mass spectrometers which computerizes results. Du Pont Instruments 109

**Catalog.** Supplement to combined annual catalog tells "What's New for the Laboratory," SGA Scientific Inc. 110

## American Society for Ecological Education

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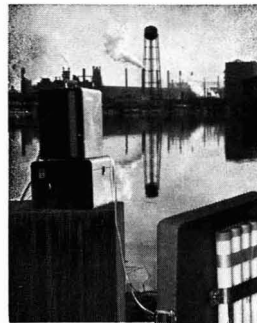
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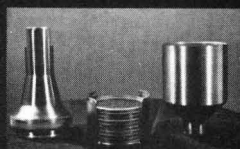
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**Hydraulic disintegrator.** New literature describes submersible oil hydraulic-drive disintegrator designed for reduction of waste water solids in deep wet wells and other areas subject to flooding. BIF SaniTrol, Inc. **111**

**Specs.** Data sheet No. FGB 30 gives description and complete specifications on a new gas-fired straight stack fume incinerator for air pollution control. Ross Engineering Machinery Division **112**

**Sampling cells.** Data sheets illustrate the range of macro, micro, and ultramicro infrared cells for liquids, mulls, and gases. Information details wide choice of pathlengths, volumes, and transmission characteristics for cells. Barnes Engineering Co. **113**

**Flowmeter.** Bulletin describes Mag Pipe 1100 magnetic flowmeter. Literature covers transmitters with solid-state components, integral and remote transmitter options, test set for on-location systems check, and field servicing capabilities. Taylor Instrument Process Control Div. **114**

**Water pollution control.** Company offers illustrated brochure entitled "The Most Economical and Effective Method of Water Pollution Control" describing holding reservoirs lined with reinforced rubber sheeting. Plymouth Rubber Co. **115**

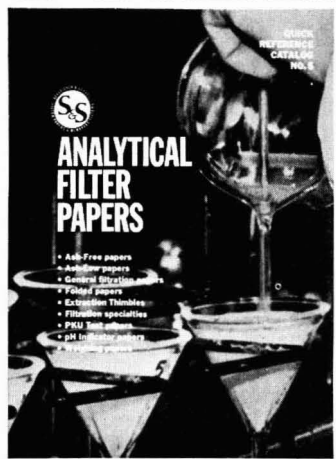
**Pollution control services.** Bulletin summarizes company's offerings in consulting, research, and engineering services related to solid waste disposal and control of air and water pollution. Bolt Beranek and Newman Inc. **116**

**Environmental indices.** "Oak Ridge Air Quality Index" describes method for providing citizen with objective evaluation of air quality. ORNL-NSF Environmental Program, Oak Ridge National Laboratory, Oak Ridge, TN 37830 (Write direct)

**Solutions to auto pollution.** Booklet for public consumption details work of company in developing catalysts to reduce automobile emissions. Englehard Minerals and Chemicals Corp., Murray Hill, NJ 07974 (Write direct)

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# bookshelf

**Proceedings SOS/70: Third International Congress Food Science and Technology.** xiii + 951 pages. Institute of Food Technologists, 221 N. LaSalle St., Chicago, IL 60601. 1971. \$15, hard cover.

Included in the program agenda was a session devoted to water supply and water disposal. Covered water quality in food processing, agricultural wastes management, vegetable-canning wastes, pollution control in canning, dairy waste treatment, and reuse of waste water in food production. ■

**Pesticides in the Environment, Vol. 1, Part 2.** Robert White-Stevens, Ed. 358 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, NY 10016. 1971. \$28.50, hard cover.

Compendium presenting properties, functions, utilities, and contributions

of pesticidal chemicals. Brings together the concepts of experts from various specialized disciplines related to pest control through the carefully metered, correct, and approved use of registered chemicals. Intended for all soil scientists, chemists, biochemists, soil microbiologists, and other scientific fields as well as government officials, teachers, students, and ecologists. ■

**Pollution Control Companies, U.S.A.** v + 239 pages. Noyes Data Corp., Park Ridge, NJ 07656. 1972. \$24, paper.

Intended as a guide and directory to present burgeoning industries in environmental control. First section lists companies manufacturing products or providing special services, such as sewer pipe cleaning. Second section lists companies providing professional services, such as consulting, design, engineering, or analysis. ■

**Radioactivity in the Marine Environment.** ix + 272 pages. National Academy of Sciences, 2101 Constitution Ave., Washington, DC 20418. 1971. \$12.50, hard cover.

Report provides an account of what has been learned about radionuclides in the marine environment since NAS published a report in the same general area in 1957. Though specifically addressed to radioactivity in the marine environment, many concepts can be applied to other wastes discharged into the marine environment such as: industrial wastes, municipal sewage, pesticides, nutrients, heavy metals, and heat. ■

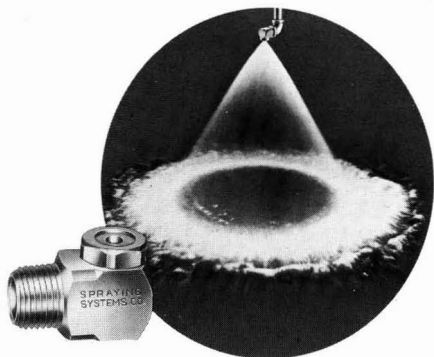
**Enzymes and the Environment.** John M. Wood. vii + 36 pages. Bogden & Quigley, Inc., 19 N. Broadway, Tarrytown-on-Hudson, New York, NY 10591. 1972. \$1.95, paper.

To be used as supplement to chemistry courses. Designed to introduce the student to fundamental principles involved in enzyme catalysis. Deals with how a variety of pollutants interact with enzymes to cause problems in metabolism. "This treatment of ecology at the molecular level is designed to stimulate the student's interest in the area of environmental science," says the author. ■

**The Limits to Growth.** Dennis L. Meadows, Donella H. Meadows, Jorgen Randers, William W. Behrens III. 208 pages. Universe Books, 381 Park Ave. South, New York, NY 10016. 1972. \$6.50, hard cover.

Nontechnical report on an 18-month study of a computerized model of the global system in which man lives. The study was carried out by 17 scientists and graduate students from six nations. The keys to achieving a stable and healthy world environment, say the scientists, are control of growth in both population and production and rejection of the myth that earth's resources are infinite. Intended as an analysis of current trends, their influence on each other, and their possible outcome. ■

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(Continued on p 376)

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Part 2: 1972 300 pages \$14.95

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*Sanitary and Public Health Engineer*

This new volume applies sanitary science and engineering principles to environmental control measures. It offers a comprehensive, up-to-date treatment of environment-related diseases, environmental engineering planning, the control of air, land and water pollution, food protection, and related programs.

1972 816 pages (approx.) 225 illus. *In Press*

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**Volume 2: Industrial Toxicology and Environmental Pollution and its Control**

Edited by **I. M. Kolthoff**, *University of Minnesota*,  
**Philip J. Elving**, *University of Michigan*, and  
**Fred H. Stross**, *Shell Development Company*

OUTLINE OF CONTENTS: Industrial Health Hazards (*H. B. Elkins and L. D. Pagnotto*). Odors (*Amos Turk*). Analysis of Air for Pollutants (*J. P. Lodge, Jr., and J. B. Pate*). Analytical Chemistry in the Control of Water Treatment Plants (*F. B. Taylor*). Potable and Sanitary Water (*R. C. Kroner and D. G. Ballinger*). Analysis of Industrial Wastewaters (*K. H. Mancy and W. J. Weber, Jr.*). Sewage, Effluents, and Sludge Analyses (*R. L. Bunch*). Subject Index.

1971 597 pages 26 illus. \$24.95

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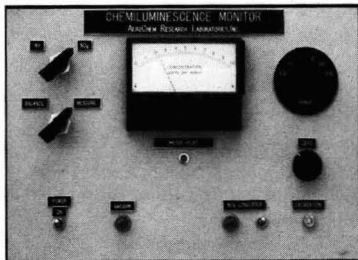
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(Continued from p 374)

**State of the Art: 1971 Instrumentation for Measurement of Particulate Emissions from Combustion Sources—** Volumes I and II. G. J. Sem et al. 415 pages. National Technical Information Service, U.S. Dept. of Commerce, Springfield, VA 22151. 1971. \$3.00 each, paper.

Volume I, intended for use as a reference guide, is written for the engineer or planner who needs to know a few basic facts about a particulate mass measurement technique in minimal time. Volume II is an in-depth report on operating principles, techniques, historical data, and discussions of the more viable techniques for particulate mass monitoring. ■

**Pollution.** Leland Stewart and Wentworth Clarke. 123 pages. The John Day Co., Inc., 257 Park Ave. South, New York, NY 10010. 1971. \$2.75, paper.

One of the Priorities for the 70's series. Deals with the consequences of the various forms of pollution—air, water, and solid wastes—if they are not curbed and analyzes the proposed solutions for averting these disasters. ■

**Treatise on Urban Water Systems.** M. L. Albertson, D. C. Taylor, L. S. Tucker, Eds. 850 pages, Publications, Engineering Research Center, Colorado State University, Fort Collins, CO 80521. 1972. \$12.50.

Based on a 1970 Institute at Colorado State University, the treatise addresses subjects related to systems and optimization techniques applied to urban water problems. Of interest to engineers and managers of urban water facilities. ■

**The WC Transportation System.** M. Leath Gray. 47 pages. Exposition Press Inc., 50 Jericho Turnpike, Jericho, NY 11753. 1971. \$4.00, hard cover.

wc, "Who's crazy?" represents the author's criticism about attitudes involving the interest in mass transportation, and the unwillingness to abandon vested interests. The wc system is a unified network of rail transport using small, car-sized units which can operate singly or in long connected series, according to need. ■

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### DETERMINATION OF AIR QUALITY

Edited by **G. Mamantov**, *University of Tennessee, Knoxville*  
and **W. D. Shults**, *Oak Ridge National Laboratory, Tennessee*

An introduction to air pollution control, this book begins with reviews of previous findings concerning such topics as storage and handling systems and surveillance networks. It explores such avant-garde topics as determination of odors and important intersocietal efforts aimed at standardizing analytical procedures in the area of air quality control. The Proceedings of an ACS Symposium held in Los Angeles, California, April 1-2, 1971.

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0-306-30571-2 \$13.50

### ALSO:

#### ENGINE EMISSIONS:

##### Pollutant Formation and Measurement

Edited by **George S. Springer**  
and **Donald J. Patterson**, *The University of Michigan, Ann Arbor*  
Approx. 430 pages July 1972  
0-306-30585-2 \$28.50

### BIOCHEMICAL ECOLOGY OF WATER POLLUTION

By **Patrick R. Dugan**, *The Ohio State University, Columbus*  
159 pages January 1972  
0-306-30540-2 \$14.50

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**April 19-21**

**Houston Junior Chamber of Commerce**

5th Annual National Pollution Control Conference & Exposition  
Houston, TX

Write: Aubrey Lafargue, Junior Chamber of Commerce, Houston, TX 77000

**April 20-21**

**International Association for Pollution Control**

Annual Conference on Pollution Control and the Marine Industry  
New Orleans, LA

Conference will cover legislation, regulations, standards, enforcement procedures, research and technology, and future concepts for environmental conservation. Contact: Carolyn Bloch, International Association for Pollution Control, Suite 700, 4733 Bethesda Ave., N.W., Washington, DC 20014

**April 20-21**

**Univ. of Tenn. Dept. of Civil Engineering and APCA Southern Section**

Second Annual Industrial Air Pollution Control Conference  
Knoxville, TN

Topics include foundry furnace, chemical processes, wood products, mining and manufacturing, and combustion process control; emerging rules and regulations for stationary sources; emission inventory, point source monitoring; and emergency episode plans. Contact: Kenneth E. Noll, Conference Director, Dept. of Civil Engineering, UT, Knoxville, TN 37916

**April 20-21**

**University of Louisville and others**

Second Annual Environmental Engineering and Science Conference  
Louisville, KY

Topics include water quality, air quality, noise pollution, and environmental planning. Contact: Joseph L. Pavoni, Assistant Professor, Civil & Environmental Engineering, University of Louisville, Louisville, KY 40208

**April 24-25**

**American Medical Assn.'s Council on Environmental and Public Health**

1972 Congress on Environmental Health  
Los Angeles, CA

Contact: Diane Dale, Dept. of Environmental, Public, and Occupational Health, AMA, 535 N. Dearborn St., Chicago, IL 60610

**April 24-25**

**Du Pont Instruments**

Second Annual Symposium on Mass Spectrometry  
Wilmington, DE

Directed at pollution, food, and drug analysis. Write: T. R. Garrett, Symposium Director, Du Pont Instruments, 1500 S. Shamrock Ave., Monrovia, CA 91016

**April 25-26**

**Air Pollution Control Div. of ASME**

National Symposium  
Cincinnati, OH

Covers compliance timetables. Contact: Ted Striggles, Arrangements Chairman, Suite 16, Atkinson Sq., Cincinnati, OH 45246

**April 25-28**

**University of Kentucky**

Significance of Insect and Mite Nutrition  
Lexington, KY

Discussions in intermediary metabolism and nutritional aspects of pest management. Write: J. G. Rodriguez, Entomology Dept., University of Kentucky, Lexington, KY 40506

**April 26**

**Filtration Society of England (Midwest-USA Chapter)**

Control of Industrial Wastes Seminar II  
Chicago, IL

Discussions will cover the pollution problem, its effects, and methods of control. Contact: Sy Peale, President, The Filtration Society, Midwest-USA Chapter, P.O. Box 693, Hoffman Estates, IL 60172

**April 27-29**

**American Congress of Expositions**

ACE WEST II  
Los Angeles, CA

Environmental air management show and meetings along with four other shows. Contact: ACE WEST II, 77 Jack London Sq., Oakland, CA 94607

**April 28**

**The Chemists' Club Library**

Environmental Science Technology Information Resources Symposium  
New York, NY

Will cover sources of environmental information and the utilization of multiple sources for problem solving. Write: Simone Spoerri, Librarian, Chemists' Club Library, 52 E. 41 St., New York, NY 10017

**April 30-May 2**

**American Nuclear Society**

Executive Conference on Nuclear Standards  
Monterey, CA

Write: American Nuclear Society, 244 E. Ogden Ave., Hinsdale, IL 60521

**May 1-2**

**Oklahoma State University**

Conference on Synthetic Fuels from Coal  
Stillwater, OK

Sessions include the synthane process, COG process, S&W coal gasification, and nuclear power for coal gasification. Contact: Billy L. Crynes, Associate Professor, School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74074

# meeting guide

**May 1-2**

**Rochester Institute of Technology**

Water Pollution Problems and Effects in the Great Lakes Basin Symposium  
Rochester, NY

Write: A. Robert Maurice, Rochester Institute of Technology, Rochester, NY 14623

**May 1-4**

**Institute of Environmental Sciences**

18th Annual Technical Meeting and Equipment Exposition  
New York, NY

Will review the status of environmental sciences, integrate all aspects of environmental problems, and investigate problems associated with educating those involved in environmental decisions. Contact: Institute of Environmental Sciences, 940 E. Northwest Hwy., Mt. Prospect, IL 60056

**May 1-5**

**American Society of Lubrication Engineers**

Annual ASLE meeting  
Houston, TX

Includes a pollution control education course and technical symposium. Write: Richard Wathen, Wathen Associates, Inc., 6 E. 43rd St., New York, NY 10017

**May 1-5**

**Navy Industrial Environmental Health Center**

Workshop in Environmental Health  
New York, NY

Of interest to the medical profession, safety officers, industrial hygienists, and managers. Contact: W. A. Redman, Jr., 3333 Vine St., Cincinnati, OH 45220

**May 2-4**

**Purdue University**

27th Purdue Industrial Waste Conference  
Lafayette, IN

For more information, contact: David W. Hawkins, Civil Engineering Bldg., Purdue Univ., Lafayette, IN 47907

**May 3-5**

**Instrument Society of America (Northern Calif. Section)**

18th ISA-Analysis Instrumentation Division Symposium  
San Francisco, CA

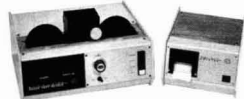
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*(Continued on p 378)*

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## MEETING GUIDE (continued)

### May 4

#### PA Technical Assistance Program and others

Air Pollution Control in the Cement Industry

Bethlehem, PA

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### May 7-12

#### Electrochemical Society

Electrochemical Contributions to Environmental Protection Symposium

Houston, TX

Contact: Ernest G. Enck, Executive Secretary, ECS, P.O. Box 2071, Princeton, NJ 08540

### May 8-10

#### American Society for Quality Control

26th Annual Technical Conference

Washington, DC

Topics will include nuclear power and environmental control. Write: American Society for Quality Control, 161 W. Wisconsin Ave., Milwaukee, WI 53203

### May 8-11

#### American Petroleum Institute's Div. of Refining

37th Midyear Meeting

New York, NY

Will spotlight steps being taken by refiners to prevent air, water, and noise pollution. Write: American Petroleum Institute, 1801 K St., N.W., Washington, DC 20006

### May 8-11

#### American Mining Congress

1972 American Mining Congress Coal Convention and Exposition

Cleveland, OH

Subjects include water treatment, sulfur reduction, dust control, and reclamation programs for surface mining. Contact: American Mining Congress, Ring Bldg., Washington, DC 20036

### May 11-12

#### Chemurgic Council

33rd Annual Conference

Washington, DC

Sessions on agricultural wastes, municipal wastes, and waste heat. Contact: John Ticknor, Chemurgic Council, 350 Fifth Ave., New York, NY 10001

### May 11-12

#### International Association for Pollution Control

Second Annual Conference on Pollution Control and the Marine Industry

Washington, DC

Conference will provide vessel owners, operators, port authorities, oil drillers, manufacturers, and legislators a total view of all present and proposed activities in marine pollution control. Write: Thomas Sullivan, IAPC, 4733 Bethesda Ave., N.W., Washington, DC 20014

## Courses

### April 15, 22, 29, and May 6, 13, 20

#### American University

Community Environmental Management Series Short Course

Washington, DC

Sessions identify and discuss the role of systems tools and techniques in confronting: air and water pollution, solid waste disposal, and other areas. \$250. Contact: Martha Sager, Director of Environmental Science Programs, American University, Washington, DC 20016

### April 17-21 and 24-28

#### University of Texas at Austin

Advanced Water Pollution Control Short Course

Austin, TX

First week covers biological waste treatment, and the second week covers physical and chemical waste treatment. Contact: Engineering Institutes, P.O. Box K, Univ. of Tex. at Austin, Austin, TX 78712

### May 4-5

#### University of Wisconsin—Extension

Water Pollution—Law & Regulation Seminar

Milwaukee, WI

Will inform engineering personnel in the executive and management areas of municipal, state, and business activities concerning laws and regs which technology will have to satisfy in the next decade. Contact: John Gammell, Engineering Extension, Civic Center Campus, 600 W. Kilbourn Ave., Milwaukee, WI 53203

### May 15-18

#### University of Massachusetts—Amherst

Environmental Quality Control—Monitoring & Analysis Procedures Short Course

Amherst, MA

Concurrent sessions measuring air, water, and noise pollution and solid wastes. Fee: \$160. For details: Course #CE 72-54, Continuing Education, Univ. of Mass., Amherst, MA 01002

### May 15-19

#### Vanderbilt University

Development of Design Criteria for Wastewater Treatment Processes Seminar

Nashville, TN

Will cover biological treatment and physical-chemical treatment of municipal and industrial waste waters. Fee: \$275. Contact: W. Wesley Eckenfelder, P.O. Box 6222, Station B, Vanderbilt Univ., Nashville, TN 37203

## Call for Papers

### May 15 deadline

#### Illinois Earth Science Association

National Symposium on Methods of Learning Environmental Science

Chicago, IL

Open to innovative studies and programs on learning environmental sciences at pre-college, college, and graduate levels. Write: Musa Qutub, Chairman, Symposium on Methods of Learning Environmental Science, Dept. of Earth Science, Northeastern Illinois Univ., Bryn Mawr at St. Louis Ave., Chicago, IL 60625

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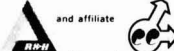
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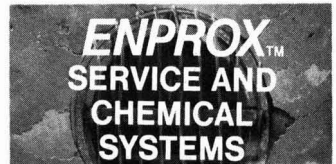
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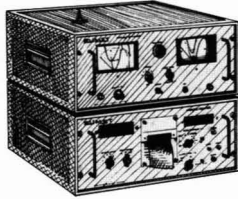
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# How To Measure Airborne Particles

## The Airborne Particle

Airborne particles are small solid or liquid objects temporarily suspended in the atmosphere. For the purpose of air pollution measurement, instruments have been designed to count and measure airborne particles in size ranges which produce health hazards (0.3 to 1.0 microns) or bothersome soiling (1 to 20 microns). The simplest of these instruments merely drives a stream of particle-laden air through a paper tape and estimates particle concentration (or "Coefficient of Haze") according to the color of the soiled spot on the tape. There is no correlation between COH and particle size distribution, . . . and air pollution health hazard standards require a combination of accurate particle concentration and size distribution data.

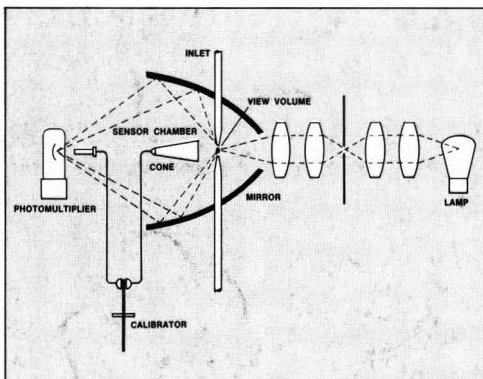


To meet these new standards, electronic particle counters based on the principle of light-scattering have been developed. These instruments measure the size of each individual particle, permitting tabulation of the relative concentrations of various sizes within the total concentration, . . . vital information for public health-oriented pollution studies.

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A continuous stream of particle-bearing air is pumped through the sensor at a fixed rate. Each particle in the stream intersects an intense beam of light, producing a



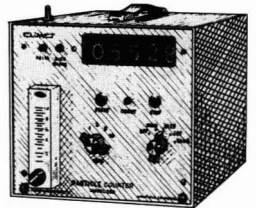
burst of scattered light energy. In the CI-201, the point of intersection is located at the primary focal point of an elliptical mirror, . . . and a photomultiplier is located at the secondary focal point. Each burst of light is transmitted directly from scattering point to photomultiplier by reflection. The elliptical mirror, which surrounds the scattering point, collects four or five times as much light energy for a given particle size than a conventional lens-type optical sensor. This advantage is particularly significant where accurate measurement of sub-micron particles is required.

## From Bursts Of Light To Data

Each burst of light is converted by the photomultiplier to a pulse of electricity. The height of each pulse is proportional to amount of light scattered, . . . a function of the size of the scattering particle. The pulses are measured and counted, and the observed data for each cubic foot of air analyzed is recorded for later statistical analysis. Climet builds a family of particle data systems, each incorporating a pulse height analyzer and display, recording and programming electronics.

## A Family Of Sensors

Particle size and concentration data is widely used in general air pollution studies, health hazard research, and enforcement of limits on industrial emissions. Climet manufactures a family of particle sensors tailored to the variety of air pollution monitoring requirements encountered by research organizations, industrial companies and public agencies.



Sensor	Performance	Application
CI-201	Analyzes 1/4 cubic feet of air per minute. Detects and measures particles as small as 0.3 micron.	Accurate particle counting and sizing for air pollution and aerosol research
CI-208	1/4 cfm flow rate, 0.5 micron sensitivity.	Clean room monitoring.
CI-250	1 cfm flow rate, 0.5 micron sensitivity.	Rugged, low-cost instrument for general purpose field monitoring.

Contact Climet for illustrated technical literature on airborne particle counters. *Climet Instruments, A Division of Wehr Corporation, 1240 Birchwood Drive, Sunnyvale, California 94086 Telephone (408) 736-6950*

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