ENVIRONMENTAL
Science & Technology

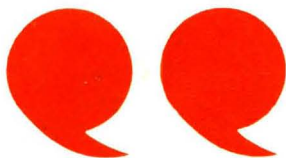*Emphasizing*
Water,
Air,. &
Waste
Chemistry

APRIL 1968
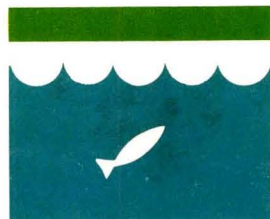
Does a fume nuisance have you cornered?

Take the only easy and sure way out.

The direct-flame method of eliminating industrial fumes and odors is the only method that's completely effective full-time—anytime. Its design efficiency never drops off.

Organic vapors and particulates are simply incinerated by an unchanging, persistent flame, day after day, year after year. A direct-flame system doesn't require constant attention, and maintenance is practically nil.

The economy of Air Preheater's Cor-Pak® Direct-Flame Fume Incinerator lies in a built-in heat recovery system. It can cut your incineration fuel bill by as much as 80%. This makes Air Preheater's direct-flame system not only consistently effective, but also an economical solution to industrial fume control.

Behind it all is Air Preheater's total design and applied research capability, that includes on-site testing with a portable unit, laboratory analysis, and odor evaluation. It all adds up to a properly engineered system that will adapt readily to process changes.

Don't get cornered by the industrial fume problem. Write Department CP81 today for your copy of a descriptive brochure.

THE AIR PREHEATER COMPANY, INC.,
Wellsville, New York 14895
A Subsidiary of Combustion Engineering

CONTENTS

It would be easy to panic and buy the wrong kind of air pollution control equipment.

Maybe you're getting more and more upset about the smoke coming out of your stack. Why not ask for expert, impartial advice? Research-Cottrell, the world's largest manufacturer of air pollution control equipment, can help you avoid expensive mistakes. We make all four major types of equipment...and we'll recommend the most economical kind to solve your problem. Fill out the coupon now. It's a good way to get rid of a big worry.

Research-Cottrell

Research-Cottrell, Inc., P.O. Box 750, Bound Brook, N. J. 08805 / Electrostatic Precipitators • Mechanical Collectors • Wet Scrubber Systems • Fabric Filters

☐ Please send me literature that contains helpful hints on air pollution control.

NAME_____

TITLE_____

COMPANY_____

ADDRESS_____

CITY_____STATE_____ZIP_____
M

EDITORIAL

Scientific community seeks environmental involvement

Choosing the most effective corrective actions to apply to environmental problems demands the nation's best minds

At the invitation of the Subcommittee on Science, Research, and Development of the House Committee on Science and Astronautics, the American Chemical Society in mid-March reported on its major study on the role of chemistry in solving the problems of the environment. The study is part of the continuing effort by the ACS to contribute, in whatever capacity, to the betterment of man; it is, further, a move by a major segment of the scientific community to get more involved.

Speaking for the ACS at the hearings was Dr. Lloyd M. Cooke, Chairman of the Subcommittee on Environmental Improvement of the Society's Board Committee on Chemistry and Public Affairs. Dr. Cooke, Manager of Planning for the Food Products Division of Union Carbide, and recently elected to the ACS Board of Directors, as part of his testimony quoted from the preface of the Society's draft report on "The Science and Technology of Environmental Improvement." Said Dr. Cooke: "Our aim in this report has been to set down in one place an objective account of the bearing of chemical science and technology on the problems of environmental quality—what is known, how it is being used, what needs to be known, how it might be used. . . . Our intent has been to focus strongly and specifically on chemistry, chemical engineering, and the related sciences, and, thereby, to stimulate the chemical awareness and the flow of chemical know-how that are essential to any long-term rational approach to understanding and managing our environment."

That the ACS, overall, seeks to ". . . initiate and conduct studies and prepare and publicize to the membership and the public reports on problems involving the role of chemistry in public affairs . . ." is obvious and well known. In addition to the report in preparation, ACS has encouraged its members to offer expert testimony to various congressional committees and to whatever government agencies, whether federal, state, or local, might find such testimony helpful.

The purpose of all these activities by the Society is to develop, through the expertise of its members and its friends, a dispassionate and constructive approach to analysis (with suggestions for solution) of the chemical problems facing today's world. One of the very special areas of chemical problems concerns the environment.

Dr. Cooke told the subcommittee (Congressman Emilio Q. Daddario, D.-Conn., Chairman) that the Society does not necessarily hold that science and technology offer a panacea for environmental improvement and control. He noted that technical facts should be made available in an unprejudiced fashion to those who must make the decisions. But, he pondered, has the Society found the best way to do this? "We must search out the proper role of a modern scientific and educational society in the context of public affairs."

The problems facing society at large are huge from an environmental standpoint alone. Indeed, the Daddario subcommittee has said: "The matters of environmental quality, with deep roots in the natural sciences, have not yet attracted sufficient attention from the scientific and engineering community. Corrective activities involve long-term commitments and high costs which provide clear motivation for additional research, development, and demonstration projects. These are problems worthy of the very best thinking we can muster."

As Dr. Cooke told the subcommittee on the Society's behalf, "It is our aim to help answer this call." ES&T applauds the statement and pledges its fullest support. With its parent organization, ES&T seeks to help the working scientist or engineer communicate with his peers and with officials at all levels and in all branches of government who must deal with the environment. In so doing we hope to contribute to the development of a rational approach to the understanding of our environment and to a coherent program for its management.

Melvin J. Josephs

Would you let your kids play in the creek behind your plant?

Water pollution *isn't* everybody's problem. It belongs mostly to the people who operate our industrial production facilities. People like you.

So what have you done about it lately?

A lot of people are taking a close look at a unique new liquid waste disposal system called Pyro-Decomposition. It's marketed by the Prenco Division of Pickands Mather & Co. and like we said, it's unique.

This patented system doesn't just change the form of your fluidized waste. It *destroys* it. In fact, once you run your liquid waste into this packaged system, that's the last you'll ever see of it. Time, turbulence and temperature (up to 3000 degrees) take it from there. There's no smoke, no odor, no visible ash, no secondary waste of any type. It's a complete, permanent solution.

The price is right, too. Compared to chemical treatment Prenco Pyro-Decomposition not only costs less but cuts disposal costs by 75%. And if you're hauling the stuff away in tank trucks, there isn't any comparison at all.

So let Prenco help you make your stream a little cleaner place for the waders of this world.

For this free booklet on Pyro-Decomposition, write today to Pickands Mather & Co., Prenco Division, 700 Penobscot Bldg., Detroit, Michigan 48226, Phone (313) 962-1560.

PM PICKANDS MATHER & CO.

ENVIRONMENTAL
CURRENTS

NCAPC Contracts for Sulfur Oxides Research

The National Center for Air Pollution Control has awarded 13 contracts for research and development to reduce sulfur oxides pollution. Twelve grants (totaling $1.06 million) are for work on developing techniques to control sulfur oxides pollution from fuel combustion. One grant, to Arthur G. McKee and Co. for $375,000, is for a systems analysis study of the primary smelter industries.

Congress Moves to Protect the Nation's Estuarine Areas

FWPCA's estuarine pollution studies

Battelle Memorial Institute

Overall national socio-economic value of estuaries, especially Chesapeake Bay

Florida State University

Apalachicola Bay

University of Rhode Island

Narragansett Bay

Texas Water Quality Board

Galveston Bay and its tributaries

Authorization for a 2-year, $1-million study of the nation's estuarine areas has cleared the House. Under the provisions of H.R. 25, the Department of Interior will inventory U.S. estuarine areas, including the Great Lakes, Chesapeake Bay, Puget Sound, the Everglades, Pamlico and Albermarle, the vast bayou country, Great South Bay, Buzzards Bay, and the long coastal waterway of the East Coast and Gulf Coast. These areas, coastal lands where salt and fresh water meet, produce approximately two thirds of the seafood consumed in this country. In the five years 1960–65, the total catch of 18 coastal species decreased 50%—from 1.4 billion pounds to 700 million pounds—according to a recent report of the American Littoral Society.

Results from Interior's study are due no later than Jan. 30, 1970. Interior's Federal Water Pollution Control Administration is stepping up its activities pertaining to the estuarine pollution study. To date, FWPCA has awarded contracts totaling $284,484 for several regional studies. In addition, the Office of Business Economics of the Department of Commerce is measuring and projecting economic activities such as population, employment, and income as they relate to estuaries and their development.

Project Skywater Reports

The cloud-seeding techniques it is perfecting, says the Bureau of Reclamation, will be able by 1985 to increase annual water supplies in the U.S. by 10% or 475 million acre-feet. Production costs will range from $1 to $4 per acre-foot, with benefits ranging from $5 to $50 per acre-foot, according to the first annual report of Project Skywater. The report predicts that operational programs will begin as early as 1972 and that by 1975 programs in the Colorado River Basin will provide as much as 2 million acre-feet of additional streamflow.

During fiscal year 1967, 26 bureau contractors were involved in Project Skywater, accounting for 90% of the program's $3.75 million budget. (The program is slated to increase to $4.5 million in 1968 and $5.5 million in 1969.) This research has uncovered some problem areas, among which the bureau lists: • Atmospheric conditions best suited for seeding. • Amount of artificial nuclei required. • Behavior of nuclei inside real clouds. • Measuring and evaluating effects of seeding. • Determining meteorological side effects. • Legal, biological, and other implications of precipitation management.

And now for the latest temperature and humidity readings,

brought to you by the best instruments made.
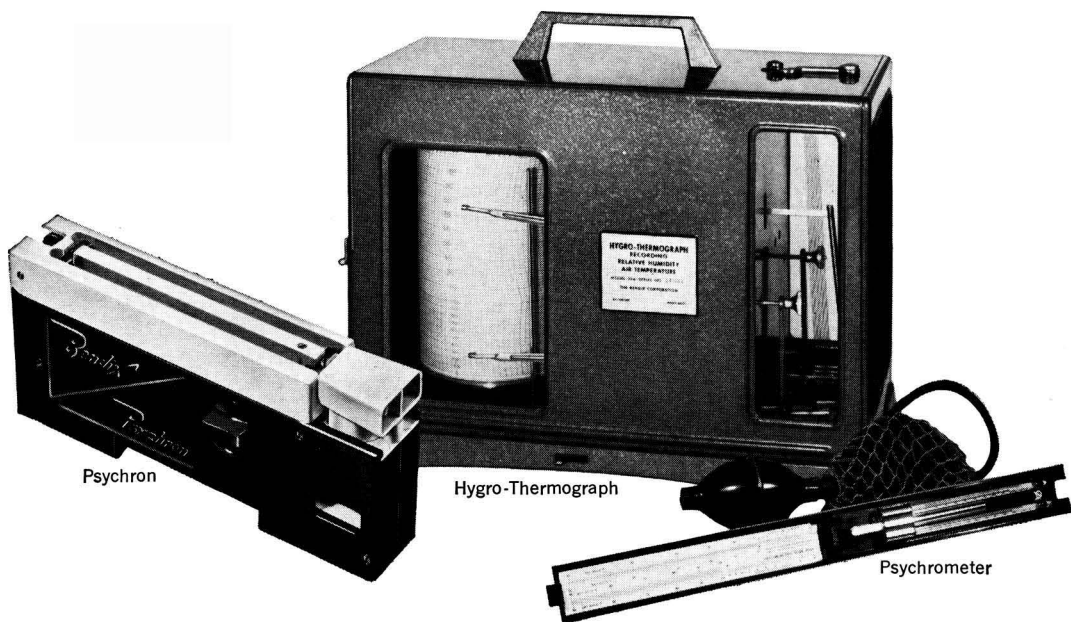
Psychron

Hygro-Thermograph

Psychrometer

If you're in a business requiring rigid environmental controls, Friez® instruments are for you. Every last one of them is as reliable, as durable and as accurate as all others should be.

Take our Psychron®, for example. It measures relative humidity via a unique wet and dry bulb setup. It's extremely accurate. It requires no whirling, so you can operate it in the closest quarters.

Or take our Psychrometer. It does everything our Psychron does and then some. Relative humidity. Dew point. Specific humidity. Mixing ratio. Vapor pressure. The works.

Finally, consider our Hygro-Thermograph. It records relative humidity and temperature simultaneously on a continuously moving chart. (Here, you can even specify daily or weekly readings. In F. or C.)

For complete information, see your supplier, or write: Dept. 81, Environmental Science Division, The Bendix Corporation, 1400 Taylor Avenue, Baltimore, Maryland 21204.

Bendix

APPROVED WATER QUALITY STANDARDS

ALASKA
HAWAII
VIRGIN ISLANDS

APPROVED IN COLOR
* SOME EXCEPTIONS   TOTAL APPROVED 29

More Controls on Pesticides . . .

The use of 94 pesticides on food and feed crops has been canceled by the Agriculture Department. Some uses of another 175 pesticides were also canceled as USDA ended federal registration on many agricultural chemicals previously accepted as leaving no residues. Such chemicals will now be registered only if it is shown they can be used without leaving a residue greater than that established by the Food and Drug Administration. The more sensitive analytical methods available now often make it possible to detect residues not detectable by methods in use when the materials were first registered. Most pesticide uses were extended when the manufacturers either petitioned to establish a permitted residue level or submitted a progress report indicating studies are under way which will permit establishing such a level. USDA anticipates no problems from the cancellations because substitutes are available in most cases. Many cancellations involve older compounds of limited use but still on the registration list.

DDT tolerances on 36 fruits and vegetables, meanwhile, are being decreased. FDA and USDA find that the present tolerance of 7 p.p.m. is higher than necessary for adequate pest control. Actual amounts of DDT residues have been well below this level in the past 4 years. One group of 24 commodities will now be limited to 1 p.p.m., another group of 12 to 3.5 p.p.m. All DDT tolerances are to drop to 1 p.p.m. beginning with the 1969 growing season. FDA studies show that the daily intake of DDT by people in the U.S. is well below the 0.6-mg. limit set by the Food and Agricultural Organization and the World Health Organization.

. . . And on Carbon Tet, Too

FDA also moved to ban carbon tetrachloride from interstate commerce. The ban would cover the chemical alone and in mixtures, as well as its use in fire extinguishers. The extinguishers are now banned in federal and some state institutions and buildings. FDA feels that since many safer substitutes are available, carbon tetrachloride is an unnecessary hazard.

Water and Sewage Service for More Rural Americans

Nearly 1.2 million rural Americans acquired modern water and sewer systems in 1967 through loans and grants from the Farmers Home Administration. A total of $212.1 million went to 1146 small rural communities (less than 5500 population) to construct or improve facilities. This is a record year for the program; in 1966, $184.5 million went to 960 communities. Most communities depended on wells, cisterns, springs, or water hauled in by truck for their drinking water, and on pit privies or cesspools for waste disposal. FHA estimates that 33,000 small communities in the U.S. are still without good water supplies, and that at least that number are without sewage service.
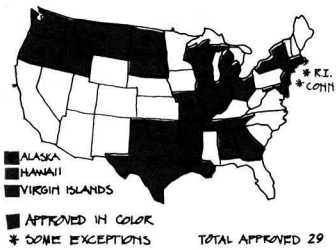
Auto Scrap Tested as Cores in Building Blocks

Concrete blocks molded around compacted automobile scrap show promise of utility in the construction of light commercial buildings, bridge abutments and piers, foundations, and retaining walls, according to the Bureau of Mines. Under a BuMines contract, Korblock Corp. (Hornell, N.Y.) made cylindrical blocks 2 feet in diameter and 4 feet long and rectangular blocks 2 feet by 4 feet by 1 foot. The blocks are lighter than solid concrete blocks of similar size, and—because of their porous centers—provide better insulation. In tests with Lehigh University's 7-story-high press, walls of scrap-cored blocks bore a load comparable to the ultimate strength of those constructed with solid masonry. To make the blocks, car bodies are first burned; the scrap metal remaining is cut into sections, compressed, and encased with 2 inches of concrete which is steam-cured using heat from the burning process. Metal accounts for more than half the volume of the block. Korblock thinks the blocks can compete in the building materials market and is making plans to build a pilot plant.

Philadelphia's Emissions Drop in the Past Decade

Pollutants (tons per day)	1968	10 Years ago
SO₂	721	830
NO₂	298	300
Organics	565	1,350
Particulates	188	470
CO	(2,619)	(data not available)

Each day 1200 tons less pollutants are discharged into Philadelphia's air than 10 years ago, says Mr. Larry Himmelstein, acting chief of the Air Pollution Control Section of the Philadelphia Department of Public Health. The emissions include sulfur dioxide, nitrogen dioxide, organics, and particulates only, according to the preliminary report made available at last month's meeting of the Philadelphia Air Pollution Control Board. The sources include transportation, domestic fuel, commercial fuel, fuel for electrical power generation, industrial fuel, industrial processes, and refuse disposal. Although Philadelphia's emissions sources are discharging less pollutants than 10 years ago, Himmelstein says that it does not necessarily follow that Philadelphia's air is less polluted than 10 years ago. It merely means that Philadelphians are contributing less to their pollution load than previously.

Organic Air Pollutants Separated for Evaluation

An atmospheric dust sample containing more than 1 kg. of organic matter has been separated into a series of reproducible fractions. Using a series of extractions, Pressure Chemical Co. of Pittsburgh separated water-soluble, acidic, basic, and neutral fractions. The neutral fraction was further separated by chromatographic columns into aliphatic, aromatic, and 10 oxy-neutral fractions. The fractions will be used to establish health effects and toxicity of air pollutants. Pressure Chemical, under contract with the National Center for Air Pollution Control, developed the procedures from laboratory scale techniques set forth by the Public Health Service for use with less than 1-gram quantities of organic starting materials.

Polluters Told to Tell All

Detailed pollution information will have to be revealed at an enforcement conference or hearing, according to new regulations proposed by the Federal Water Pollution Control Administration. At request of a majority of conferees, a polluter will have to file a report identifying the character, kind, amount, and sources of discharges. Trade secrets need not be divulged. If the report is not filed in the time allotted, the polluter is notified in writing of his default. Thirty days thereafter, if the report has not been filed, the polluter will be penalized $100 a day until the report is filed.

Mathematical Models Assess Rivers Pollution Control Alternatives

Mathematical models have been used to examine the relative merits of many methods for controlling water quality in the Delaware estuary. Using dissolved oxygen as the criterion, Leonard Ortolano and H. A. Thomas, Jr., of Harvard examined the following control methods: primary, secondary, and tertiary sewage treatment plants; increase in reaeration coefficient; control of combined sewer overflows; removal of bottom deposits; and piping of wastes outside the basin for ocean disposal. They concluded that the practice of installing secondary treatment plants before considering the less conventional alternatives is a good one. However, as loads grow and secondary treatment is no longer adequate, Ortolano and Thomas say that it is worthwhile to consider the less conventional techniques as an alternative to tertiary treatment. The pipeline approach appears especially attractive and is under further study. In their research, the scientists told American Institute of Chemical Engineers at a recent meeting in St. Louis, they first used a static model with a simplified representation of estuary geometry and waste load distribution; they then went on to a more sophisticated, working model. They found that both models gave essentially identical results.

More Research on Odor Problems

The National Center for Air Pollution Control is looking for research and development groups to undertake studies assessing the social and economic impact of odors. The study will consist of two parts: In the first, a nationwide survey will be made to determine the amount, principal sources, and geographic distribution of odor problems. In the second, a selected community will be studied intensively to develop rapid and effective methods for assessing the impact of odors.

ITT Research Institute has found eight industrial sponsors for a 3-year study it is undertaking to place odor evaluation on a firmer scientific basis. The study will use an olfactometer developed by the institute to determine the threshold at which humans begin to smell given odors. The olfactometer can also determine the amount of one odor vapor that can be added to another before members of a test panel notice a significant change in odor.

Health and Air Pollution
Subject of New Studies
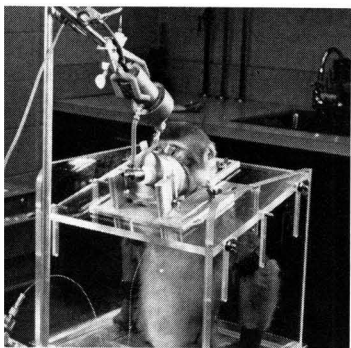
Finding answers. *To bridge the gaps in our knowledge of the effects of long-term low-level exposure to various pollutants, rhesus monkeys at Hazleton Laboratories are tested for pulmonary function after pollutant inhalation*

One controversial aspect involved in setting standards and managing the air environment is that the experts cannot agree on the effect air pollution has on man's health. Laboratory studies are one way of trying to find out. Early studies opted for the simple and inexpensive—small rodents were exposed for short periods to high concentrations of single pollutants. What this means for man, who is exposed for long periods of time to low concentrations of pollution mixtures, has been the subject of considerable debate.

Better answers may be forthcoming from two projects now under way at Hazleton Laboratories, Inc., Falls Church, Va. Costing upward of $3.8 million, these projects will determine the biological effects on monkeys of low concentrations of various pollutants and mixtures of pollutants, for relatively long periods.

The first study, under way for about a year, is financed primarily by Edison Electric Institute and National Coal Association; the second, in progress for three months, is financed by American Petroleum Institute. The studies are similar in experimental details but differ in the pollutants involved and what the studies are trying to determine.

The EEI-NCA study is intended to provide data useful in setting criteria for the three most conspicuous pollutants emitted from stacks of coal-burning plants. They are:
- Sulfur dioxide, a gas.
- Sulfuric acid mist, a droplet aerosol.
- Fly ash, a particulate aerosol.

Monkeys and guinea pigs are being exposed to these pollutants at levels actually measured in polluted urban atmospheres. Different groups of monkeys will be exposed in three consecutive 1½-year cycles. Deciding on a time period was a particularly difficult problem, according to Harold N. MacFarland of Hazleton, who is in charge of the studies.

"We wanted as long a period as possible," Dr. MacFarland points out. "At the same time, the urgency of the pollution problem requires answers as soon as possible. And, of course, longer periods cost more money. This 1½-year period represents 6% of the monkey's normal 25-year life span—you might compare it to 5 years in man.

"The guinea pigs will be exposed for four 1-year cycles, which represents a much larger percentage of their normal 2–3 year life span. Another factor is the extensive testing we're doing on the animals. We feel we're going to recognize any changes very early," he says.

MacFarland also decided to test only normal, adult animals. "We know from the Donora-type incident that the very young, the very old, and the respiratory cripples react more strongly to air pollution. Studying such special populations would be a logical extension of our study on healthy animals. In fact, the sponsors have expressed an interest in just such studies."

Experimental design

When the test animals arrive at Hazleton, they spend the first 2–3 months becoming accustomed to their new surroundings. They are also tested extensively to get base line data on each animal.

In each cycle, cynamolgus monkeys will be tested in 11 groups of nine each. Each group is housed in a six-foot cube chamber on an around-the-clock basis. If we allow for feeding and testing the animals and cleaning the cham-

OUTLOOK

Monkeys exposed to low levels of pollutants for long periods of time may give a better idea of how man is affected by breathing polluted air

bers, daily exposures run 18–22 hours.

The pollutants and concentration ranges selected for the first cycle of monkey tests are:

• *Sulfur dioxide* (four chambers):
0.1 p.p.m.
0.5 p.p.m.
1.0 p.p.m.
5.0 p.p.m.

• *Sulfuric acid mist* (four chambers):
0.1 mg./cu. m., in two particle sizes—less than 1 micron and 1–5 microns.
1.0 mg./cu. m., in two particle sizes—less than 1 micron and 1–5 microns.

• *Fly ash* (two chambers):
0.1 mg./cu. m., in particle size distribution found in postprecipitator fly ash.
0.5 mg./cu. m., in same size distribution.

• *Control group* (one chamber).

Hartley strain guinea pigs are being exposed in four chamber, 140 per chamber. Exposures are to sulfur dioxide at 0.1, 1.0, and 5.0 p.p.m.; the fourth chamber is the control group.

"We're using the guinea pigs for several reasons," MacFarland declares. "They'll give us a point of comparison, since most earlier studies were done on guinea pigs. Secondly, if qualitative and quantitative reactions are similar in both species, we'll be safer in making the species jump from monkey to man. And, finally, guinea pigs are especially sensitive to respiratory irritants, so we should be able to detect more subtle changes."

Testing techniques

To detect these changes, Hazleton is using more than 50 different procedures—among them chest x-rays, electrocardiograms, growth data, and several standard hematological and biochemical measurements. But special emphasis will be placed on a battery of tests that determine three specific types of lung function:

• *Mechanical properties.* About three dozen different tests will be used. The techniques available in this group are the most numerous because they were the first type to be developed. These procedures measure such things as elasticity of the lung, the resistance to air flow, and how much work is involved in breathing.

• *Ventilation properties.* Six to eight tests are used to determine how effectively the lungs move air in and out.

• *Diffusional properties.* Two or three tests determine how effectively oxygen and carbon are diffused across the lung membrane to the blood stream.

Most tests are run about every two weeks, before, during, and at the end of the exposures.

To handle these amounts of data, Hazleton is using an on-line IBM 1800 computer. Tests are performed and results recorded; the information goes to the computer, which analyzes the data and feeds the results back in seconds.

At the end of the cycle, the animals will be sacrificed and all major tissues and organs examined.

The second cycle will start two or three months after the first one ends. This delay allows time for the research workers to finish analyzing the results of the first cycle, to design the next cycle, and to acclimatize the next group of animals. The second cycle

For the next five years, Hazleton Laboratories Inc. (Reston, Va.) will be looking at the effects of air pollutants on laboratory animals, including guinea pigs and monkeys. By exposing and measuring the reaction of test animals to controlled atmosphere and analyzing the data by computer as they proceed, Hazleton aims to find what health effects, if any, long-term exposure of pollutants has on these animals.

Sponsored by the Electric Research Council, the $2.25 million study at Hazleton is designed to gage some of the biological effects of pollutant emissions from large, coal- or oil-fired, electrical power plants.

At present, test animals are being exposed to sulfur dioxide and fly ash, contaminants produced by coal burning power plants Throughout the test, the animals are being checked by computer to see whether their respiration is being affected and, if so, how much. This long-term analysis will not be complete before 1971, so conclusive results on health effects from air pollutants still remain a controversial subject for research. Realistic concentrations of pollutants are emphasized in this study, according to Dr. Harold N. MacFarland, Director of Hazleton's Inhalation Division.
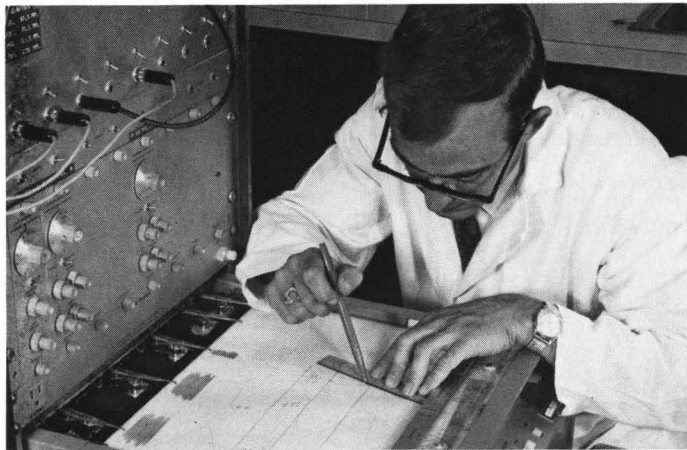
Laboratory animals that have spent their entire lives breathing polluted air show few effects traceable to pollution, according to Dr. Ralph G. Smith, Department of Occupational and Environmental Health of Wayne State University's School of Medicine.

For the past five years continuous checks were made on two test colonies of rodents consisting of rats, guinea pigs, and rabbits. One group breathed ambient polluted air; the other group only air purified by activated carbon filters. Some animals were both born and raised in the laboratory and then examined at their natural death.

"One of the few indications of any changes due to air pollution was a small increase in the white blood count of the exposed group —a condition that does not imply deterioration in health," says Dr. Smith. He explains that the body's white blood cells normally increase to attack foreign materials, which would explain the higher count for the exposed group.

Although the study did not support the contention that breathing polluted air, at the measured levels, is harmful to health, Dr. Smith cautions that extrapolation of these findings to humans must obviously be made with caution. Humans have a more sophisticated respiratory and filtering system than rodents have.

will be mostly mixtures of two pollutants, the third and fourth mostly mixtures of three pollutants. In all, 30 systems will be studied in monkeys, 12 in guinea pigs.

Originally, the study was to require 5½ years and $2.2 million. Those figures have now increased to 7 years and $3.3 million. "Such studies are unprecedented," MacFarland declares, "and we just didn't allow enough time —particularly in the build-up period. The contract was signed in June 1966, but it was almost a year later before we started the first cycle."

MacFarland at the moment is not sure where the money is coming from. "Discussions are under way with the Public Health Service, which has been observing the studies since they started. Industry has made a substantial commitment, and we hope PHS will see its way clear to do the same. We really feel this should be a cooperative undertaking," he says.

API, Hazleton, and synergism

The second study Hazleton plans is sponsored by the American Petroleum Institute. The API study will emphasize the possible role of synergism in air pollution. According to MacFarland, "Present toxicological evidence cannot explain the great number of deaths that occurred in the London, Meuse Valley, and Donora episodes of acute air pollution. The concentrations of pollutants measured weren't high enough. Indeed, the pollutants themselves are not intrinsically lethal."

One explanation of this anomaly is that gases in polluted air dissolve in

droplets or are adsorbed on particulates. In this carrier form the gases are transported into deeper lung spaces than they might normally be. Released in these areas, the gases form spots of local high concentration.

A likelier explanation, in MacFarland's opinion, is synergism.

The Hazleton study for API will cover five air pollutants at various concentrations:

* Carbon monoxide, 20, 30, 45, and 67.5 p.p.m.
* Nitrogen dioxide, 0.5, 1.2, 2.9, and 7.5 p.p.m.
* Sulfur dioxide, 0.5, 1.3, 3.7, and 10.0 p.p.m.
* Lead chlorobromide, 0.6 mg./cu. m.
* Calcium sulfate, 10 mg./cu. m.

Lead chlorobromide, a particulate, is the main lead compound found in exhaust of automobiles using leaded gasoline. Calcium sulfate is typical of "particulate sulfate" found in urban atmospheres.

The API study will require 3½ years and $1.6 million. It involves 20 chambers (9 monkeys each) with 2-year exposures, plus 20 chambers (100 rats of the Charles River strain each) with 1-year exposures. These chronic exposure studies were preceded by acute exposure trials to help get indications as to which of the pollutant combinations appear to be most promising.

The two sponsors have agreed to pool data from the studies, MacFarland says. "The mixtures in the Edison Electric Institute and National Coal Association study are pertinent to the synergism studies. And the API results on sulfur dioxide interest EEI-NAC."

Operating under the goal of producing automobiles that are virtually smog-free "compared with other sources of urban pollution," but that at the same time meet consumer requirements for performance, cost, and comfort, Ford Motor Co. and six petroleum companies have joined in a $7 million cooperative research program. Fifteen research projects comprise the Inter-Industry Emission Control program (IIEC), which was launched last April by Ford and the Mobil Oil Corp. Later the pair were joined by five other petroleum concerns—American, Atlantic Richfield, Marathon, Sohio, and Sun.

The 15 projects are split into four major areas of investigation—changes in engine systems, disposable catalysts in converter systems, semipermanent catalysts, and high-efficiency reactors. According to William D. Innes, Ford vice president (Ford is project manager of the group), all approaches are being given equal emphasis until research and engineering data have been evaluated.

The program is well under way, with 13 of the 15 projects in progress. Innes reports that the project is fully staffed, research equipment and test facilities are installed, and projects have been assigned to member companies.

Among other activities reported by the group to date are:
• Some 60 fuel additives have been screened in test engines and data have been accumulated on combustion improvement.
• Experimental exhaust recirculation systems are being evaluated for performance, durability, and drivability.
• An experimental catalyst used in a chassis dynamometer study may reduce hydrocrabon and carbon monoxide emissions.
• Flame and nonflame reactors show favorable initial readings.
• Fuel-injection technology is under study.

Information generated from the program will be made available to industry, according to IIEC, and under certain conditions interested companies other than the present participants may still join.
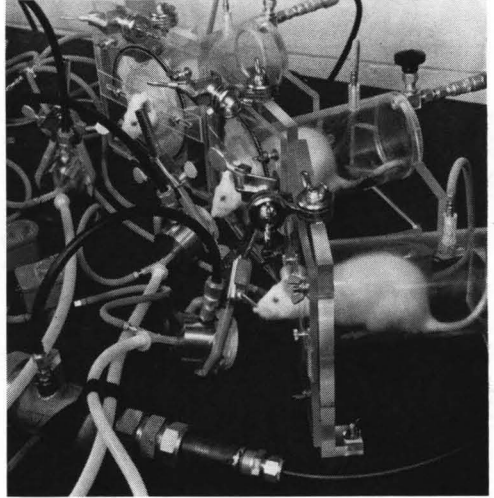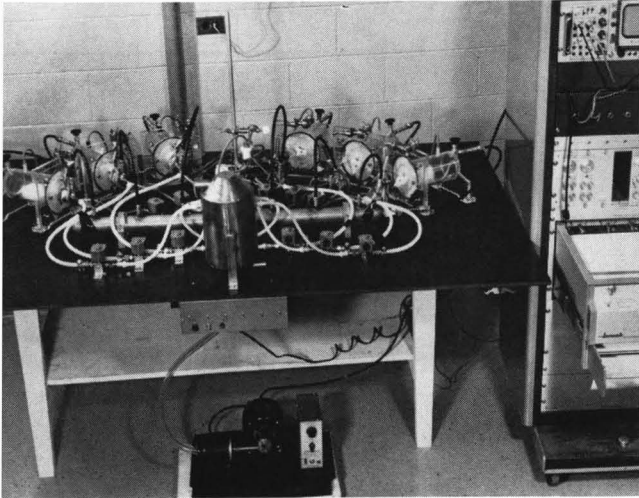
Inhalation studies. *A semiautomatic plethysmograph system (top, left) measures the lung function of six rodents simultaneously as they are exposed to air pollutants and toxic gases*

Close-up. *Guinea pigs and monkeys, as well as the white rats shown here (top, right), will be monitored for their reactions to pollutant exposure*

Housing. *The chambers (left) for the monkeys, who will be exposed to sulfur dioxide and fly ash in the initial studies, have been specially designed for the Hazleton experiments*

Abel Wolman...
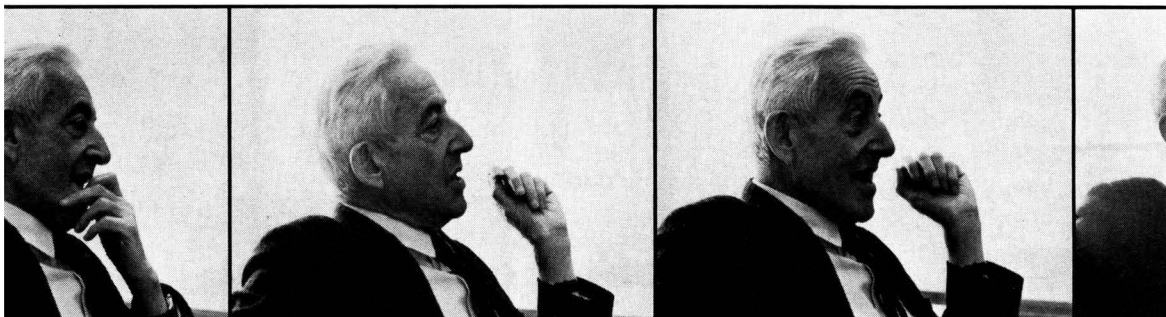
Abel Wolman can look back on a career spanning more than a half century, a half century that has seen the United States grow from a nation of 92 million people—about half living in rural areas—to an industrialized nation of 200 million, with almost 70% living in urban areas. Throughout, Wolman, now professor emeritus of sanitary engineering at Johns Hopkins University, has been intimately involved in what today is called the quality of the environment.

Since his retirement, the pace of Wolman's activities has, if anything, increased. "Now that I'm retired, everyone seems to think I have a lot of time on my hands," he says. "As a result, all sorts of things keep coming my way. I'm lucky, though. Now I can pick only those things that interest me."

As consulting engineer from 1963 to 1967, he helped set up water and sewage organizations for the metropolitan Detroit area. "There are a lot of challenging issues facing us today," he declares, "and I want to have my hand in them."

Consulting plus serving on advisory groups are his principal endeavors. He spends about half his time traveling. Last year he visited Russia, Taiwan, England, and Alaska. India, Kenya, and Europe are tentatively scheduled on this year's agenda.

When not traveling he walks daily across Baltimore's Charles Street to his office at Hopkins. "Twenty years ago when my wife and I built our house, we sold our car," Wolman says. "Neither of us has driven since, but we have no problem getting where we want to by bus or cab. Our son, who is head of Hopkins' geography department, thinks I'm just waiting for the automobile to prove itself. But when I served on an advisory group to Baltimore's public transportation problems, I had a lot of first-hand experience—more than the president of the local transit company, who rarely used the bus."

A group considering the problems of Medicare and Medicaid has just been added to Wolman's list of advisory activities. The group, appointed by the Governor of Maryland, is composed of a cross section of citizens, including doctors, bankers, businessmen, and hospital administrators

Wolman joined the U.S. Public Health Service after receiving a B.A. degree from Johns Hopkins University in 1913. He received a B.S.E. degree from Hopkins in 1915 and an honorary doctorate in engineering in 1937. From 1914 until 1939 he served the Maryland State Department of Health, the last 17 years as chief engineer. From 1937 until he retired in 1964, he was professor of sanitary engineering at Hopkins.

Throughout his career, Wolman has advised various government agencies. He has been chairman of both the Maryland Water Resources Commission and the Maryland State Planning Commission. For many years he was chairman of the
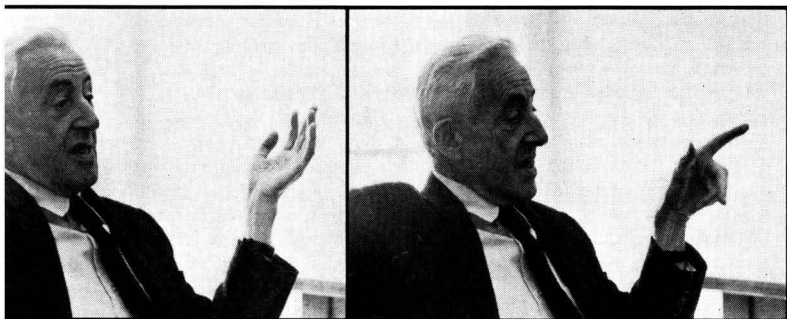
talks about...

National Water Resources Committee of the United States.

He has also been advisor to many federal agencies, including the Atomic Energy Commission, the Tennessee Valley Authority, Defense Department, Office of Science and Technology, Geological Survey, and Public Health Service.

He was with the advisory group that first grappled with the pollution problems of the development of nuclear power. "This is a good example," he says, "of how a need develops an entirely new technology. Nothing originally available could clean up stacks to the degree atomic power plants require, so technology developed the materials and techniques to meet that specific need. I think this kind of thing will continue to happen as we try to improve our pollution control programs."

Through his consulting, Wolman's influence has also been felt at the local level. He has been consulting engineer to Balti-more, Detroit, Columbus, New York, Seattle, Portland, and other cities, assisting not only in design of plants but also in setting up managerial organizations to cope with pollution problems in general. As consulting engineer for the World Health Organization, he has traveled to Ceylon, Taiwan, India, Ghana, Brazil, Chile, Argentina, and Israel.

Wolman is a member of the National Academy of Sciences and the National Academy of Engineering. He served as president of both the American Public Health Association and the American Water Works Association; and for 18 years he edited the *Journal of the American Water Works Association*.

This article was prepared by the editors of ES&T from a recorded interview with Dr. Wolman that was arranged and conducted by Norman Metzger, producer-director of "Men and Molecules," an ACS News Service feature.

❝...European answers to American problems ❞

It always interests me to hear someone say we should look at what Europe is doing in the pollution area. This is an astonishing suggestion to those of us who have actually seen conditions in the Ruhr, for one example. The conditions there are not acceptable now in this country—and certainly will not be in the improved situation we're trying to create.

The Ruhr, put together with the Emscher, is a creek, compared to our river basins—the Ohio, the Hudson, the Susquehanna, the Potomac. In the Ruhr they're running the water ragged —reusing, reusing, and it's pretty sloppy at the end. The Emscher is literally an open sewer. It's so bad they're building a plant to treat the entire river. What kinds of examples are these for us? We do better than that.

Another illustration of the pitfalls of applying European answers to American problems is the burning of garbage to produce electricity. This is being done quite widely in Europe, particularly in West Germany.

There are probably only a couple of plants in the whole United States doing this now. Atlanta has had such an operation for a great many years, with the electrical power plant adja-

cent to the incinerator. We considered this in my own city of Baltimore a number of times. But the locations on which we could put an incinerator were so far removed from the power plants, that no one was willing to put in the necessary pipelines.

Another factor is the amount of heat produced in the average incinerator. It's a drop—if I may mix up my analogies—in the bucket with respect to the job that, say, Con Edison has to do in New York.

Or, take a look at the Scandinavian countries where they recover a low-grade fertilizer from garbage by composting. (Incidentally, the operation is subsidized.) But it makes sense there. They are intensive farmers and need any kind of fertilizer, including low-grade.

Business Week recently described the composting plant in Altoona, Pa. What the article didn't say is that Altoona is having problems with its plant: They're running out of space in this little community of 70,000. Second, the plant is losing money. And, third, they can't get anybody to take the stuff.

Now what does this mean to New York City, with its little problem of

8 million people? Where would you compost in such a metropolitan area? Imagine the hauling involved. It is just a completely impractical, uneconomical thing to do.

Europe does have one thing that I think we should copy—and which we are already doing on a small scale. This is a managerial institution in which industry is represented and has a voting role. This is good. Europe's so-called user charge is also a good idea, although it is greatly misunderstood in this country. It is not a penalty for polluting—it is much like the sewer service charges we've had in our country for at least a quarter of a century.

In thinking of these things, there's one important difference you must keep reminding yourself of. The difference holds true if you're thinking of producing electricity from incineration of garbage, of recapturing fertilizer values from garbage, or of salvaging materials from garbage. Europe must do all those things.

The United States simply has no use for it. It's a wasteful procedure as we do it. But we have no economic reason for doing otherwise, and we will not have for a long time.
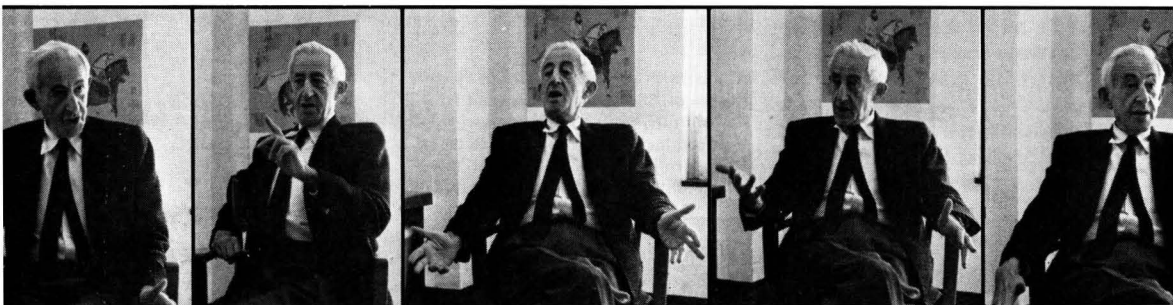
❛...reuse and history repeating itself ❜

I should remind you that this country has been all through a salvage and reuse period. If you will follow my evolution for a moment, you'll see why we sit where we do today.

In the twenties, many American cities used reduction plants to recover grease and low-grade fertilizer from garbage. It was about a fourth grade chemical industry, the most miserable I've ever seen. New York did it; Philadelphia did it; Boston, Pittsburgh, Chicago, and Baltimore, too.

After many court cases, they all closed. (In those days, I spent a lot of time in court—I was then chief engineer of the Maryland State Department of Health.) Those plants closed because they were a mess, in the stack and on the ground. We spent years trying to treat the stacks, and if anything made them worse.

I remember the famous Yandell-Henderson process, which came, as I remember it, out of Yale. The process was supposed to chlorinate odoriferous materials in the stack. We tried it in Baltimore, and the odor would knock you down.

The reduction plants closed for another reason. Our experience in Baltimore will explain why. We went through a cycle of which most people today making all those pronouncements on the whole salvage business are completely unaware.

We closed in Baltimore because we ran out of customers. We had one big customer, Procter & Gamble. They used to pay us 2½ to 3 cents a pound for grease, which went into their glycerine process. During the first world war, the price rose to 36 cents, and they'd take everything we could give them. Of course, it was not a very good product, and when the war ended they found something better. The price dropped back down to 3 cents, or thereabouts, and soon we couldn't give the grease away.

We couldn't give our fertilizer away either. We recaptured glass. Molten metals, too. I remember we had a manufacturer in Baltimore who took our molten metal to make sash weights for windows. At one time, he'd take all we had. Then he started using springs in the windows instead. Nobody else would take the metal. We were out of business.

Piggeries were another phase of the early days of garbage disposal in this country. They made sense. Garbage has organic food. Why throw it away? We can use it to raise pigs.

Los Angeles did it in the twenties and even the thirties, by hauling garbage out to the desert. At one stage, I guess Los Angeles had 25,000 to 30,000 hogs—and that's a lot of hogs. At first contractors paid Los Angeles for the stuff. That was the millennium! Pretty soon, contract renewals were dropping. Next thing, Los Angeles had to pay the contractors. Finally, the contractors quit altogether.

The garbage was no longer good enough, so it had to be supplemented. Such things as refrigeration, household disposers, and packaging improvements made the garbage less valuable organically. And, because of the disease problem in hogs, antibiotics had to be added. The whole thing just worked itself out.

And in that period, barging garbage to sea was practiced by many coastal cities. New York City did this. Its contractor was supposed to dump beyond Ambrose Light. But—particularly in storms—this wasn't being done. A great deal of New York's garbage was ending up on the Jersey beaches. I recall sitting in the courtroom and being able to read a Delmonico menu card that had been
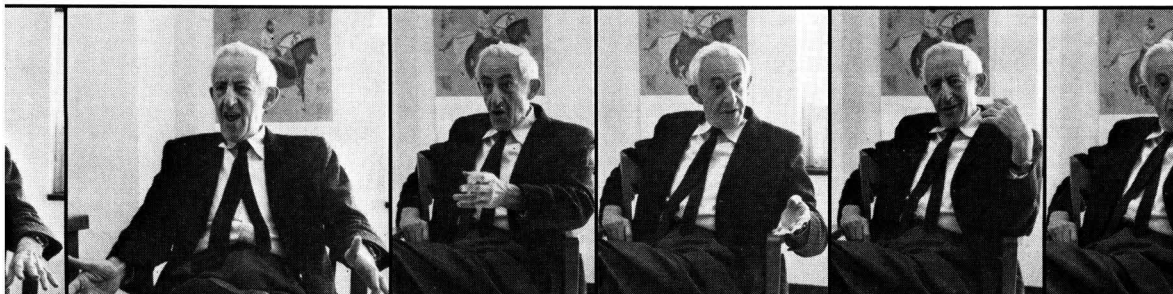
thrown out in New York's garbage and ended up in Atlantic City. The State of New Jersey brought suit and the Supreme Court put a stop to that practice.

Sewage sludge is another example of the way this reuse cycle has worked in the past. Back in the fifties, Milwaukee got a lot of publicity when it began making fertilizer from sewage sludge. Milorganite, as it was called, was great stuff for things like golf links. At one time, it was going for $40 to $60 a ton. But four or five years ago, when the plant was supposed to be doubled, the decision was made to discontinue production entirely—for very obvious reasons. It never paid. It never paid for operation, much less for capital investment.

There's another aspect to this problem, too. In the forties, San Diego began to produce a better fertilizer—that is, higher in nitrogen and phosphorus —from activated sludge. Then everybody thought, "Well, if that's so great, we'll produce, too." The result was that the entire market disappeared. One plant could produce enough for

the entire Pacific Coast. You see, it still wasn't really good fertilizer.

One hope was that truck farmers could mix it with regular fertilizer to make soil more friable. But because of urbanization, this kind of farmer is no longer really close to the cities. It just wasn't economic to haul such low-grade material those distances.

I don't want to leave you with an overly pessimistic view of the possibilities of salvage or reuse. We will move increasingly into reuse of both liquid and solid materials—when necessity warrants it.

Look at reuse of waste waters. It's as old as the hills in the United States. It is only new to the present commentaries. In almost every one of our major river systems, waste waters are reused, with a great deal of skill, with a great deal of success, and with a great deal of economy.

The direct reuse of sewage water after purification has also been practiced in the United States. In Baltimore, we have the largest reuse of municipal waste in the world. We've

done this since 1942 with great success. I refer to Bethlehem Steel's reuse of all treated sewage waste water from the Baltimore metropolitan area.

This proved possible for a couple of reasons. First, Bethlehem needed large amounts of industrial water. Second, Baltimore's sewage treatment plant is sufficiently close to Bethlehem's integrated system to combine the two. Bethlehem takes about 125 million gallons of waste water a day, and will continue to take the increasing amounts we'll be sending them in years to come. Baltimore makes about $100,000 a year in the arrangement.

This sort of thing will be done increasingly, but only when it's profitable to do so. It's being done in Los Angeles. In fact, I recommended it almost a quarter of a century ago, but things were not ripe for it then.

Just two years ago I made a similar recommendation to Israel, which is short of water. Instead of running their municipal waste out to the sea, I suggested putting it back in the sand dunes. Then they could take it out later as well water.

❛... surprises in algal growth❜

The next few years may bring a great many surprises concerning the probable causes of algal growth. The symposium last year at the University of Wisconsin corralled a fair body of scientific opinion from around the world.

The general conclusion of those scientists with great experience was that we don't know really what the cause is. They cautioned that you had

better not put all of your eggs in that phosphate-nitrate basket. This matter has tremendous impact on decision-making in the estuaries, which is certainly one of our great problems.

About two years ago a group at Johns Hopkins reviewed the estuaries problem. The conclusion was that we did not know what would happen if we removed all phosphates from upstream. We doubted that it would

help. Yet, literally millions of dollars are being pressured into that particular field.

But this doesn't mean we can't act. We can. We know a great many things to do, and we should do them and increase the pace at which we do them. But for heaven's sake, we mustn't get ourselves in a corner where we really have no idea of what we are talking about.

❛... congressional committees and growing expertise ❜
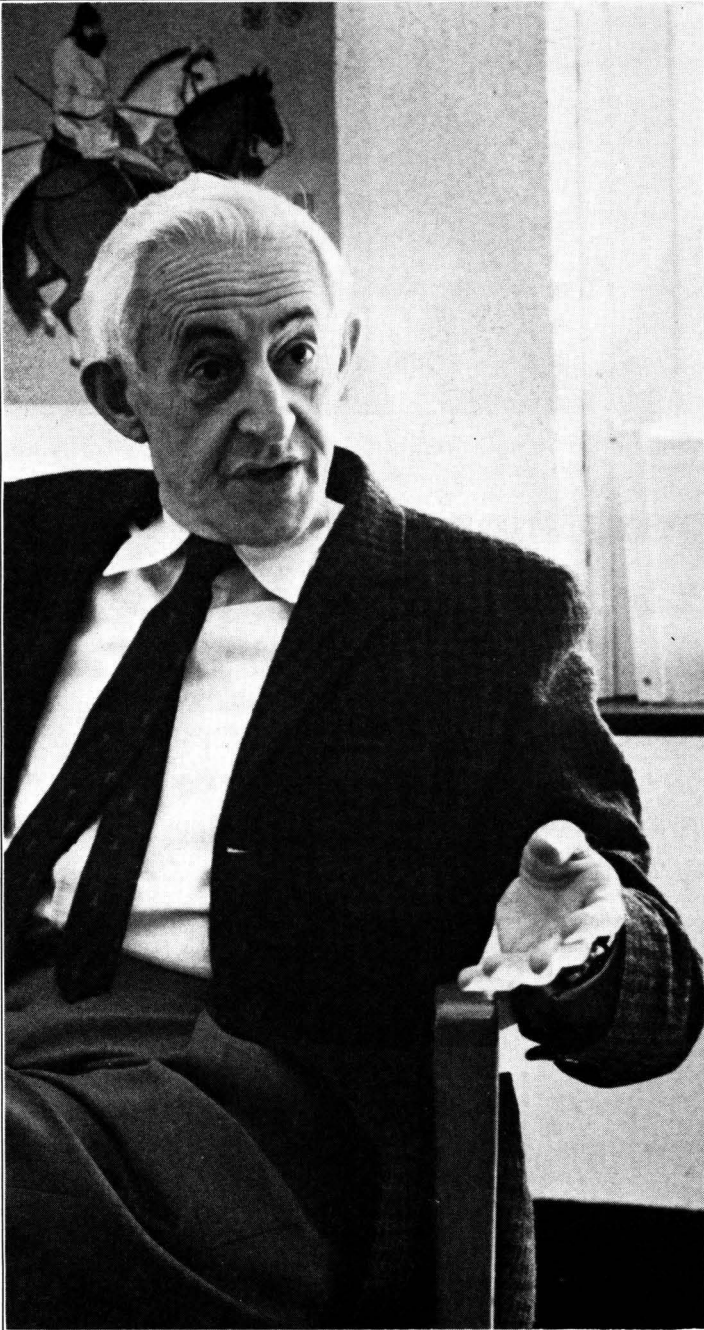
There's a lot of talk these days that pollution isn't being corrected fast enough because of problems at the local level. I simply remind everybody that long before federal interest became great, long before federal grants came into being at all, the municipalities in the United States were doing a job of tremendous size. They were spending $1.2 to $2.0 billion annually for water and sewage treatment.

The federal effort has now brought on an interesting situation. Federal spending is highly variable—right now, it has fallen to quite a low level. What is happening now is that municipalities are holding back, waiting for bigger federal grants. "The grants now are only 30%," they're saying. "In a year or two they may climb to 50 or 75%; don't push me." And, of course, they're right.

The entire grant-in-aid method, it seems to me, has a built-in penalty. As I have indicated in congressional testimony, I would like to see a substitute for this method, for administrative reasons. My own state, Maryland, is a tiny state. Still, last year we had something approaching 275 separate federal grants for one purpose or another. This drives us crazy, as it does everyone else in the United States.

I am one of those who would like to see a gross return to states and municipalities, by whatever formula the Federal Government wants. The totals could very well work out to what we now get, but administratively would be much simpler to use. The federal objection is that the problem areas might not be upgraded. I say this could be written into the specification. Perhaps the total could be apportioned—so much to air pollution, so much to schools, and so on.

Whoever heard of a university establishing a separate office for just federal paper work—but that's what Johns Hopkins has had to do. What it means is that a lot of the money goes into administration, and not into the project itself. We ought to be ingenious enough to come up with a better solution than that.
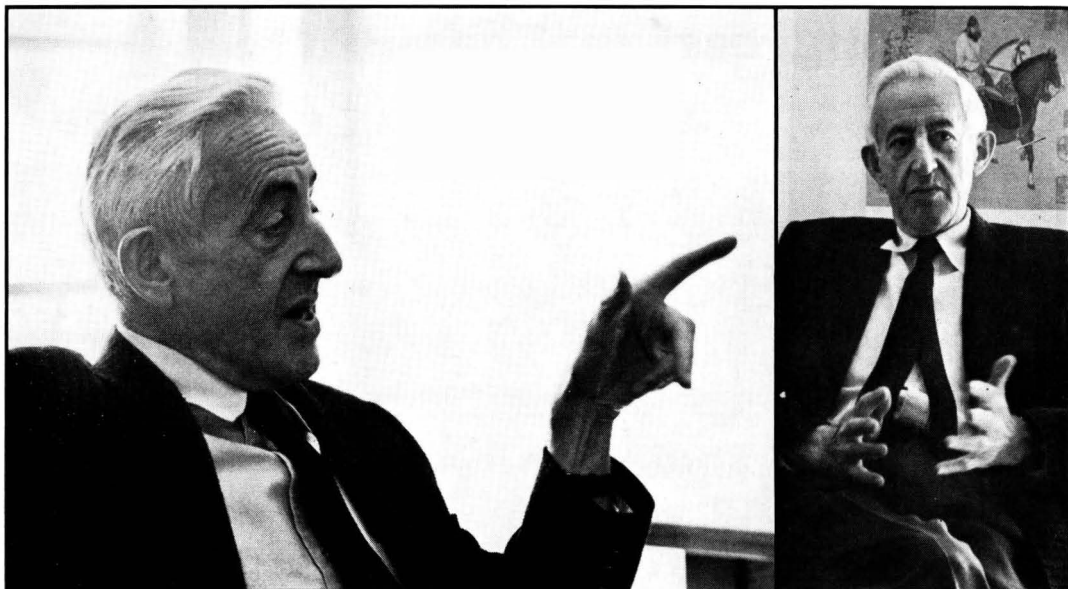
❝ ...local problems
and the federal presence ❞

My activity on the federal level dates back to about 1934. In fact, I chaired the first congressional committee that made a report on pollution. That was about '36 or '37. We spelled out what we thought the Federal Government ought to be doing. It did, in fact, do much of what we suggested within a few years.

I would say that in general the congressional process is a much improved technique over what it was 30 years ago. First of all, its public hearings are far more extensive. Committee staffs have improved tremendously —in both numbers and quality. And the committees get superb support from the Library of Congress reference group.

This is a noiseless operation, but a very effective one. I have a lot of dealings with them, and I am amazed at what they can do in the way of summoning up source materials, expert opinion, witnesses, and appropriate questions.

The committee members themselves have become extremely savvy. Witnesses appearing before the House Committee on Science and Astronautics, particularly before the Daddario subcommittee, are not appearing before novices. The same is true of the Joint Committee on Atomic Energy. It's almost 20 years old now. Chet Holifield has been sitting on the committee all of those 20 years. He knows what he is talking about. What's more, he knows when you don't know what you are talking about.

I predict these committees will get even better at getting at the bottom of these complex situations involving major public policy. How fast this happens depends on the willingness of scientists and technologists to cooperate, on their knowledge, and on their ability to help clarify some of the issues.

*National needs and costs of
water pollution control,
directed at 10 major industrial groups,
gets careful scrutiny in new Interior report*

The Cost of Clean Water

Cost of water pollution control in the U.S. gets careful scrutiny in a voluminous report released recently by the Department of Interior. The report, "The Cost of Clean Water," deals with Interior's study of the national requirements and costs of water pollution control. Prepared in response to a requirement of the Federal Water Pollution Control Act, the three-part report is directed at 10 major industrial groupings:

- **Blast furnaces and steel mills.**
- **Motor vehicles and parts.**
- **Paper mills.**
- **Textile mill products.**
- **Petroleum refining.**
- **Canned and frozen fruits and vegetables.**
- **Leather tanning and finishing.**
- **Meat products, including poultry.**
- **Dairies.**
- **Plastics materials and resins.**

Congress directed Interior "to conduct three studies—one, a study of the cost of carrying out the Federal Water Pollution Control Act, as amended; another, a study of the economic impact on affected units of government of the cost of installing waste treatment facilities; and the third, a study . . . of the national requirements for and the cost of treating municipal, industrial, and other effluent to attain water quality standards established pursuant to the act of applicable state laws."

This first annual report, which covers the fiscal years 1969–73, must be updated and submitted to each new session of Congress. Although Secretary of the Interior Stewart L. Udall, notes that it has been impossible to arrive at a completely definitive estimate of required costs, he is quick to point out that he hopes the report will stimulate discussion. From such discussion or review, Udall feels certain that next year's report will be vastly improved and refined.

Because of the wide diversity among major industrial groupings of water need, water use, and water disposal, the report considers the 10 major industry groups in great detail. Nonetheless, Interior was able to draw some generalizations about industry.

For example, of all water used in the U.S., industry uses half, of which 90% goes for cooling. Furthermore, most of the cooling water is discharged without treatment into nearby streams, rivers, or lakes.

In terms of strength and volume, manufacturing wastes are approximately three times as great as those of the nation's sewered population. Moreover, the volume of industrial production giving rise to these industrial wastes is increasing at the rate of 4.5% per year, the report points out.

For fiscal years 1969–73 the investment for capital outlays required of the major industries to meet water quality standards will probably fall within the range of $2.6 to $4.6 billion. These outlays include the following three components:

- Meeting current needs (costs estimated to run $1.1 to $2.6 billion).

- Accommodating industrial growth through fiscal 1973 ($0.7 to $1 billion).

- Replacing equipment ($0.8 to $1 billion).

Because of increasing construction costs, however, the costs for the five-year period could expand to the range of $2.9 to $5.1 billion. During this same period, the outlay for operation and maintenance of these facilities could easily reach $3.0 to $3.4 billion.

Industry, notes the report, will have to provide a level of treatment for its industrial wastes equivalent to secondary treatment of sanitary wastes—85% removal of normal five-day BOD and all settleable or suspended solids.

These industrial waste profiles for 10 major industries in the U.S. were developed as an integral part of the national requirements and cost estimate study required by law. The profiles are a comprehensive analysis of the requirements and costs of treating wastes to attain the prescribed water quality standards. The profiles:

- Describe the source and quantity of pollutants produced by each of the 10 industries.

- Give information on costs and alternative methods of operation.

- Describe old methods changes in processing and treatment.

The profiles are a generalized framework that both Interior and Congress hope will stimulate industry to find more efficient and effective ways to reduce wastes than those that are generally practical today.
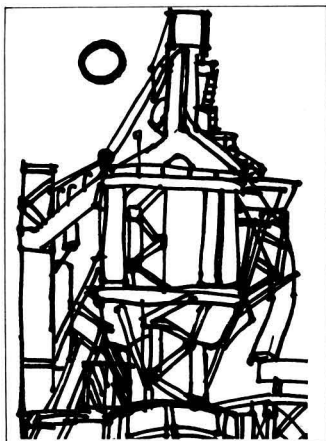
Industrial waste waters differ

Many industrial wastes differ markedly in chemical composition and toxicity from wastes found in domestic sewage. Often, the BOD or solids content is not an adequate indicator of the quality of industrial effluents. Frequently, industrial wastes contain persistent or refractory organics which resist secondary treatment procedures that are normally applied to domestic sewage. Some industrial effluents require the stabilization of specific organic compounds or the removal of trace elements as part of the pretreatment method required before the effluents are disposed to municipal sewers.

In general, industry prefers the use of municipal facilities. Although only 7.5% of the total waste waters of major industrial establishments were disposed of to municipal sewers in 1964, municipal treatment provided the principal handling method for the following industries—food processing, textiles, rubber and plastics, machinery, electrical machinery, transportation equipment, and miscellaneous manufacturing. Whereas the wastes of these industries are amenable to treatment at municipal plants, the wastes from the other four major industrial groups—paper, chemical, petroleum and coal, and primary metals—are not.

Cooperative plants develop

Many cooperative municipal-industry waste treatment plants have been scaled—or are being scaled—to handle the organic wastes of the pulp and paper, chemical, and other large using industries. For example, in Bound Brook, N.J., a chemical plant treats municipal wastes, reversing the usual relationship between industry and community. In Kalamazoo, Mich., three medium sized paper mills and one chemical plant use a modern municipal sewage treatment plant.

The industrial plant must carry out a series of required pretreatment measures before disposing of its wastes to municipal sewers. But it is equally important that the municipality maintain constant surveillance of raw waste loads to be sure that such pretreatment measures have been taken.

Blast furnaces and steel mills

The principal waste from the blast furnace operation is solid material suspended in the waste water from washing furnace exit gases free of suspended solids. Similar wastes from sinter plant operations are usually part of the blast furnace department. To a large extent these wastes result from air pollution abatement measures, although blast furnace gas must be cleaned to permit its use as a fuel.

Significant water-borne wastes result from almost all steel mill manufacturing operations. The volumes of these waste waters are unique among industrial wastes in that they are so great. These wastes are principally suspended solids, lubricating oils, heated water, waste acids, plating solutions, and dissolved organic chemicals.
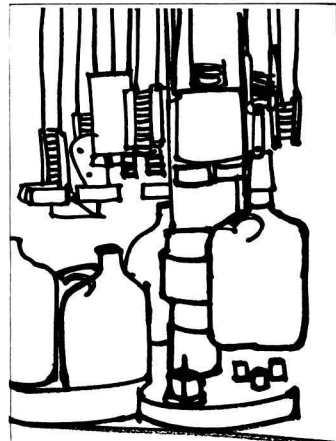
Depending upon the particular operations in which these wastes are generated, they can appear in the effluent in different combinations and, accordingly, require different methods of treatment. For example, suspended solids from blast furnace gas-washer water and sinter plant effluents are removed by either plain sedimentation or by coagulation and sedimentation. Suspended solids from hot-rolling mills are removed by the same two methods but with the additional provision for removing flotant oil by skimming. Suspended solids from cold mill effluents also are removed by these two sedimentation methods, but first the oil emulsions must be broken, usually with magnetic separators. Lubricating oils are generally removed by allowing adequate time for flotation, then skimming the oil from the water surface.

By far, spent pickling solutions are the most difficult waste water problem of the blast furnaces and steel mills industrial category. These solutions, consisting of various acids and the iron salts of these acids, result from various cleaning operations. Although spent pickling solutions and coke plant wastes can be discharged to municipal sewers and treated with municipal wastes, the practice is not widely followed in the industry. Instead, the wastes are disposed of in deep wells, reused by regeneration techniques, or neutralized with base. Deep well dis-

posal is finding increasing use and is often the least costly method of disposing of waste acids.

The trend in the steel industry is toward the use of subprocesses which yield products of lighter unit weight at increasingly higher speeds with minimum manual operations. Particularly difficult waste problems arise from some of these newer methods. In general, the subprocesses representative of the newer technologies produce greater water-borne waste loads than the older manufacturing methods. However, because the newer installations generally incorporate waste treatment facilities in their design, the actual plant discharges are not necessarily greater in the newer plants.

In 1966, the annual expenditures for waste treatment were as follows:

Cost component	Amounts in 1966	Per ingot ton
Direct	$90,104,000	$0.667
Indirect	53,875,670	0.398
Credits	53,601,860	0.397

Direct expenditures for waste treatment are approximately 0.65% of the direct expenditure for production.

Motor vehicle industry

Existing and projected waste loads and treatment practice have been established for only that part of the motor vehicle industry that is characterized as stamping plants and body and final assembly operations. Although in 1966 these three operations accounted for less than 5% of the total plant operations, they accounted for 70% of the total industry's employees and close to 23% (35 billion gallons per year out of a total 148 billion gallons per year) of the total water intake by the industry.

The pollutants usually associated with these plants are oil, heavy metals, cyanide, suspended solids, alkalies, acids, and solvents. The operations of the stamping plants produce no significant liquid processing wastes per se. The waste waters from the body and final assembly plants are mostly organic waste waters that contain suspended solids, originating primarily from painting and paint sanding.

Typically, the major body paint booths contribute 50–75% of the chemical oxygen demand and 40–60% of the suspended solids in the total waste load. Heavy metals such as zinc and chromium may also be present.

In general, changes in production processes will not materially affect the volume of waste waters nor the cost for treatment by this industry in the five-year fiscal period 1968–73. Although electrostatic painting could contribute a 50–70% reduction in COD and 40–60% reduction in suspended solids, this process will not be widely used by the motor vehicle industry before 1977.

In 1966, this industry discharged 91.2 million gallons of waste water to municipal sewers. At a service charge of 20 cents per 1000 gallons then, the motor vehicle industry paid out $5.5 million for treatment of its waste in 1966.
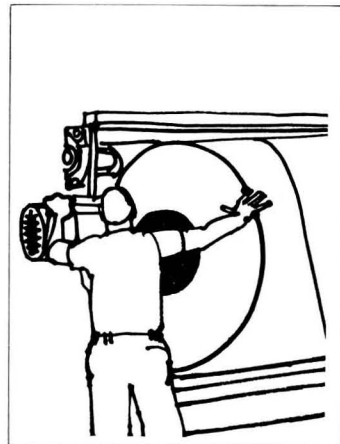
Paper mills

Derived from data from nearly 45% of the total pulp and paper mills in the U.S., the pulp and paper profile reveals that discharge of untreated pulp and paper mill effluent to municipal treatment plants—common practice in 1950—is now practiced by only a small percentage of the industry. Combined industrial and sewage treatment facilities can operate successfully when the industrial waste waters are pretreated. Pretreatment includes neutralization, addition of antifoam agents to reduce the foaming tendency of industrial waste waters, control of sulfur compounds to eliminate malodors, and reduction of suspended solids concentrations.

The discharge of this industry's waste waters to municipal sewers is expected to increase, especially when the treatment plant is designed to handle the combined waste waters. However, the tendency is still to locate pulp and paper mills in rural areas close to raw material sources.

During 1963–67, only 10–15% of the mills discharged their effluent into municipal sewers. One important factor that must be considered in any proposal to combine treatment of these waste waters with sewage is the relative flow and organic loading between the two types of waste water. If the industrial waste water is a small portion

of the total flow to the municipal system, the industrial waste water would not be expected to have a significant effect on the performance of primary and secondary sewage treatment facilities. On the other hand, if the industrial waste water is a significant portion of the total waste water flow, then specific account must be taken of the treatment characteristics of the industrial waste water in terms of design and prediction of performance of the combined waste treatment facilities.

In 1966 the replacement cost for waste water treatment facilities in the total industry was $217 million. Operating costs for specific treatment equipment are not available. However, annual operating costs range between 7–20% of the total capital investment in treatment facilities.

Textile mill products

Because of the large amounts of water required in washing and rinsing operations, water usage in the textile industries is relatively high compared to other industrial categories. Cotton and wool finishing mills use from 30 to 70 gallons of water to finish 1 pound of cloth. Synthetic finishing mills use considerably less water—anywhere from 3–20 gallons per pound of cloth.

Wool finishing wastes are high in BOD, solids, and grease content. Wool grease requires pretreatment for BOD removal before biological treatment of the plant effluent is feasible. This need for special treatment causes an especially difficult economic problem because the cost of removal of this special BOD is more than the market value of the recovered grease.

Not nearly so strong as wastes of the wool mills, cotton finishing wastes have no grease, a relatively low solids content, less BOD than wool wastes, and usually high color content. These wastes can be treated by existing biological treatment and present no special disposal problem.

Synthetic finishing wastes are different and generally lower in pollutant quantities than cotton finishing wastes. One major difference between the two wastes can be the presence of metallic ions from the synthetic treatment. These metallic ions can, in some cases, retard or prevent biological waste treatment. Thus, some kind of chemical pretreatment of synthetic finishing wastes is usually required prior to biological treatment or discharge to municipal sewers.

Costs of waste water treatment in the textile industries are a small portion of the total production costs. The Interior report estimates that the costs for waste water treatment for the entire industry are 2.0% of the total product cost for wool, 1.7% for cotton, and 2.2% for synthetics.

The net pollution from cotton finishing operations, largest producer of wastes in the textile industry, was approximately 270 million pounds of BOD in 1967. The contribution from the wool industry, according to the report, came to 130 million pounds. The contribution from the synthetic fibers industry totalled 106 million pounds. These numbers reflect the differences between the waste generated by the industries and the waste removed by industrial and municipal waste treatment plants.

The Interior report goes on to predict that a 50% decrease in the 1963 volume of discharged waste for the cotton industry will occur by 1977. Similarly, in 1977 the net volume of wool wastes will probably decrease steadily to 75% of its 1963 value. On the contrary, because of the tremendous growth rate of the synthetic textile industry, an increase in the net volume of waste discharged should reach a peak in 1968, and then decrease gradually by 1977 to its 1963 level.
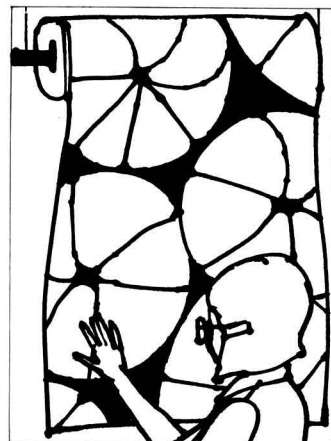
Petroleum refining

Petroleum refining, one of the largest wet processing industries in the U.S., involves some 20 separate processes which are necessary to the production of this industry's principal products from crude oil.

Total water used in U.S. refineries, including recycle, increased 48.5% for the 10-year period 1954–64 to an average daily usage of 16.8 billion gallons. Approximately 90% of this amount went for cooling purposes. During the same period, the water intake increased by only 13.2% which, Interior says, indicates a substantial increase in water reuse.

BOD, phenol, and sulfides are the major pollutants in this industry's waste waters. Two significant waste streams for the industry are the sour waters (containing sulfides and mercaptans) and the spent caustics. Almost without exception, waste waters from the petroleum refineries exert a major, and sometimes severe, oxygen demand, the primary sources of BOD being soluble hydrocarbons and sulfides.

The combination of small leaks and inadvertent losses that occur almost continuously throughout a complex refinery can become principal sources of pollution.
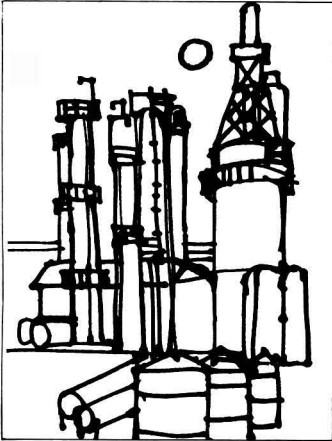
The greatest potential for waste reduction by inplant processing changes lies in improvement of general operating and housekeeping practices rather than in changing processes or subprocesses. Additionally, however, hydrocracking and hydrotesting, two processes that generate much lower waste loadings than the processes they are replacing, are being installed at a rapid pace throughout the industry. The new installations will continue to exert a strong influence on the reduction of waste loadings, particularly sulfides and spent caustics.

Almost all sewer regulations contain a provision which prohibits the discharge of oil and inflammable and explosive materials. Accordingly, only 1–2% of the process waste waters from U.S. refineries find their way to municipal sewers, according to available data presented in Interior's report.

In 1966, the replacement value and operating costs for this industry to treat its waste waters totaled close to $275 million in replacement value and $55 million for operating expenses.

Canned and frozen fruits and vegetables

The canned and frozen food industry has an annual retail value greater than $5 billion for canned foods and $3 billion for frozen food and is quite diversified. Dozens of entirely different raw and partially prepared products are processed in more than 3150 plants.

Although the frozen food industry generates approximately twice as much waste water volume per equivalent unit of production as the canning industry, the amount of pollution load generated per equivalent unit of product is approximately the same.

Eight operations—trimming, coring, pitting, cutting, peeling, inspection, grading, plus plant clean up from these operations—account for approximately 50% of the total volume of the industry's waste water, a major portion of its BOD, and virtually all of the suspended solids, the Interior report states.

In the five-year period from 1959–64, the volume of discharged waste water decreased 10% although production increased by 11%. The reason for this apparent paradox, Interior points out, is the greatly increased volume of water that is recirculated and reused. During the next 10 years, production rate for the industry will probably increase by 3%, according to an estimate of the Business and Defense Services Administration. If this growth occurs, an increase in the volume of discharged waste water will probably occur despite additional reuse of inplant waste waters.

Canning and frozen food processing wastes are largely organic and usually treated by municipal treatment plants. Nevertheless, a majority of industrial treatment plants provide minimal treatment—usually consisting of vibrating screens to remove solids—prior to discharging their waste waters into municipal systems.

Currently, municipal facilities handle nearly 62% of the cannery wastes. By 1982, municipal facilities will handle a projected 74% of these wastes, the Interior report notes. Each year municipalities are charging industries more for the use of city sewers. Both sewer use and the charge to industry are more likely to increase than decrease in the coming years.
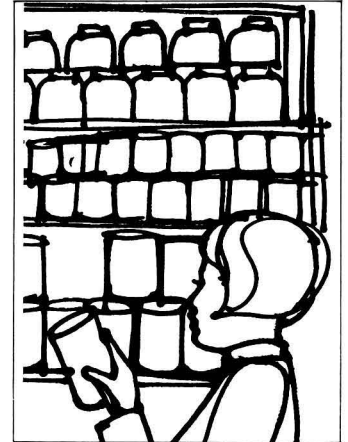
On a national basis, the canning and frozen food industry pays approximately 2% of its manufacturing costs for treatment of its waste waters. This 2% includes in-plant treatment facilities and that portion of industry's taxes attributable to municipal pollution reduction.

Leather tanning and finishing

Using 18 billion gallons of water annually, today's tanning industry is concentrated in 250 plants and amounts to a $5 billion enterprise with about 27,000 workers.

Of the 10 separate major processes of the leather tanning and finishing industry, the beamhouse unhairing process and the tanning process in the tanhouse are of major concern to sanitary engineers. Unhairing accounted for nearly one half of the total plant waste volume and BOD, and these wastes are usually highly alkaline, milky-colored, and laden with sulfide. Tanning liquor wastes accounted for only 5% of the total BOD and volume, are highly colored, and contain a large amount of solids.

Data based on 1963 experience show that a typical tannery produced approximately 1000 gallons of waste and 9.0 pounds of BOD per 100 pounds of hide processed. Approximately 700

Estimated percentages of industrial waste water discharges to municipal sewers[a]

Industry	Breakdown	1950	1963	1967	1972	1977
Blast furnaces and steel mills		2%	3%	5%	5%	5%
Motor vehicles and parts	Body and final assembly only		50	55	60	
Paper mills		5–10	10–15	10–15		
Textile mill products	Wool	34	40	60	70	75
	Cotton	20	30	35	40	
	Synthetics	35	45	50	55	
Petroleum refining				Less than 1–2		
Canned and frozen fruits and vegetables	Canned	50	60	62	65	69
	Frozen	20	25	26	30	35
Leather tanning and finishing	Tannery wastes	60	70	75	80	
Meat products	Meat packing	35	50	70	80	85
	Poultry processing	50	70	72	76	80
Dairies	Butter, cheese, and milk	1	5	10	32	53
	Ice cream, frozen desserts, and fluid milks	50	70	80	90	98
Plastics	Cellulosics			Essentially none		
	Vinyl		~60	~60		
	Polystyrene		>90	>90		
	Polyolefins			Data unavailable		
	Acrylics			Data unavailable		
	Alkyd and polyester resins			~50		
	Urea and melamine			Considerable		
	Phenolics			Data unavailable		
	Miscellaneous			Data unavailable		

[a] Based on available FWPCA Cost Analysis Profile

Estimated cash outlays to meet projected needs for cooling and treatment of industrial wastes

	Millions of constant 1968 dollars					Five-year total	
						Constant	1969–73 Current
Requirements	1969	1970	1971	1972	1973	1968 dollars[a]	dollars[b]
Industrial treatment plants							
New construction	$ 330–680	$ 350–710	$ 370–730	$ 380–740	$ 380–740	$1800–3600	$2000–4000
Replacement	130–120	140–160	160–190	180–230	200–270	820–970	920–1100
Subtotal	460–800	500–860	540–920	560–970	580–1,000	2,600–4,600	2,900–5,100
Industrial cooling							
New construction	300	310	320	330	330	1,600	1,800
Replacement	19	31	43	56	69	220	250
Subtotal	320	340	360	380	400	1,800	2,000
TOTAL capital outlay	**780–1,120**	**840–1,200**	**900–1,280**	**940–1,350**	**980–1,400**	**4,400–6,400**	**4,900–7,100**
Operation and maintenance requirements							
Industrial treatment plants	490–450	540–570	610–680	670–800	730–920	3,000–3,400	3,200–3,600
Industrial cooling plants	79	130	180	230	280	890	950
TOTAL cash outlay	**1,349–1,649**	**1,510–1,900**	**1,690–2,140**	**1,840–2,380**	**1,990–2,600**	**8,290–10,690**	**8,050–11,650**

[a] Constant 1968 dollars were developed by using July 1967 as the base
[b] Current dollars were developed by multiplying the constant 1968 dollar by projected cost indexes for each year over the five-year period
Source: FWPCA Cost Analysis Profile

Estimated volume of industrial wastes before treatment, 1963

Industry	Waste water (billion gallons)	Standard biochemical oxygen demand (million pounds)	Settleable and suspended solids (million pounds)
Food and kindred products	690	4,300	6,600
Textile mill products	140	890	Not available
Paper and allied products	1,900	5,900	3,000
Chemical and allied products	3,700	9,700	1,900
Petroleum and coal	1,300	500	460
Rubber and plastics	160	40	50
Primary metals	4,300	480	4,700
Machinery	150	60	50
Electrical machinery	91	70	20
Transportation equipment	240	120	Not available
All other manufacturing	450	390	930
All manufacturing	13,100	22,000	18,000
For comparison:			
Sewered population of U.S.	5,300[a]	7,300[b]	8,800[c]

[a] 120 million persons × 120 gallons × 365 days
[b] 120 million persons × 1/4 pound × 365 days
[c] 120 million persons × 1/4 pound × 365 days
Source: FWPCA Cost Analysis Profile

Total current value of waste treatment requirements of major industrial establishments[a]
(millions of constant dollars)[b]

Industry	By expert[c] estimate	By census projection
Food and kindred products	$ 740	$ 670
Textile mill products	170	170
Paper and allied products	320	920
Chemical and allied products	380	1,000
Petroleum and coal	380	270
Rubber and plastics	41	59
Primary metals	1,500	1,400
Machinery	39	56
Electrical machinery	36	51
Transportation equipment	220	160
All other manufacturing	200	290
TOTAL capital requirement	**4,000**	**5,000**
Plant currently provided:		
By industry	2,200	1,800
Through municipal facilities	730	640
Current backlog	1,000	2,600

[a] Assuming at least 85% reduction of BOD and of settleable and suspended solids
[b] All values rounded to two significant figures
[c] Based upon Industrial Waste Profiles
[d] Based upon Census of Manufacturers data and established treatment cost factors

gallons and 6.5 pounds of BOD come from the beamhouse operation; the remaining 300 gallons of waste and 2.5 pounds of BOD come from the tanhouse operation.

However, newer tannery operations, offering a 10% reduction in waste loads, produce about 900 gallons of wastes and 8.5 pounds of BOD per 100 pounds of hide processed.

About 85% of all leather is made into shoes. Of this shoe leather, 80% is used for upper shoe leather which is tanned almost exclusively by chromic sulfates and alkaline salts. The remaining 20% is used for sole leather and is tanned by the ancient method using vegetable compounds such as bark extracts. Processing of sole leather is expensive and results in highly pollutional loading. But this processing is gradually being replaced because of the rapid introduction and acceptance of sole material substitutes.

At present, tannery wastes are treated largely by screening, equalization, sedimentation, chemical coagulation, lagoons, trickling filtration, and activated sludge. Screening accomplishes about 5% BOD reduction, and activated sludge processes account for BOD reductions to 85–95%. In practice, the first five processes are performed at the tannery while the last two, trickling filtration and activated sludge treatment, are handled by the municipality in those instances of combined treatment.

At present, 75% of all tannery wastes are being discharged into municipal sewer systems, and the percentage will probably increase to 80% by 1972.

Industry's cost for treatment of its waste waters for 1966
(millions of dollars)

Industry	Breakdown	Per cent of industry's waste treated by municipal treatment plant	Cost for industry's treatment		Cost to industry for municipal treatment		Totals
			Replacement value	Overhead and maintenance	Replacement value	Overhead and maintenance	
Blast furnace and steel mill			$865.0	$90.0			$865.0 / 90.0
Motor vehicles and parts	Body, final assembly plants	60%	$15.1	$2.54	$13.0	$5.5	$28.1 / 8.04
Paper mills		10–15	$217.0	$36.0			$217.0 / 36.0
Textile mill products	Wool	40	$9.0	$5.0	$10.0	$4.0	$19.0 / 9.0
	Cotton	34	$9.5	$1.4	$15.0	$2.4	$24.5 / 3.8
	Synthetics	50	$6.0	$0.5	$10.0	$1.0	$16.0 / 1.5
Petroleum refining			$275.0	$55.0			$275.0 / 55.0
Canned and frozen fruits and vegetables	Canned	62	$18.0	$3.0	$60.0	$10.0	$78.0 / 13.0
	Frozen	24	$5.0	$1.0	$20.0	$4.0	$25.0 / 5.0
Leather tanning and finishing		75	$3.6	$0.5	$8.0	$0.8	$11.6 / 1.3
Meat products	Meat packing	70	$3.5	$3.5	$6.0		$13.0
	Poultry processing	72	$0.6	$1.0	$4.0		$5.6
Dairies	Butter	10			$0.9	$0.18	$1.08
	Cheese	10			$0.9	$0.18	$1.08
	Milk	10			$2.4	$0.48	$2.88
	Ice cream	80			$1.0	$0.2	$1.2
	Frozen desserts	80			$2.6	$0.52	$3.12
Plastic materials and resins[a]	Cellulosics	Little or none			$0.26	$0.1	$0.36
	Vinyls	~60			$1.01	$0.77	$1.78
	Polystyrenes	>90			$0.38	n.a.	$0.38
	Polyolefins	Little or none					
	Acrylics	Not available			$0.07	$0.01	$0.08
	Alkyds and poly-esters	~50			$0.19	$0.02	$0.21
	Urea and melamine	Considerable			$0.01	$0.01	$0.02
	Phenolics	Not available			$0.51	$0.41	$0.92
	Miscellaneous	Not available			$0.05	$0.02	$0.07
	Total for plastics						$2.5 / 1.32

[a] Based on 1967 data.

Assuming that the total annual number of hide deliveries remains at 32 million per year and, further, that a majority of beamhouse operations are not transferred to the slaughter house or reduced by tannery relocation adjacent to slaughterhouses, waste water volumes will decrease from 1963 level of 16.0 billion gallons to 14.0 billion gallons per year by 1982. BOD loading will decrease from 150 to 145 million pounds per year by 1982. The reduction may come about, in large part, because of the proportionately greater use of leather for upper parts of the shoe as leather substitutes find increased use for soling.

Meat products

The immediate problem of animal slaughter is the most important item in setting waste water volumes and pollution loads for the meat products industry. This is the conclusion reached from study of questionnaire data from 219 plants, 54% of which are federally inspected plants.

Of the five industry wide processes —blood recovery, paunch handling, edible rendering, inedible rendering, and cleanup—which account for the waste load impact of the meat packing industry, blood recovery is by far the most important. Total blood recovery —practiced by more than 95% of the industry in 1966—means a 42% reduction in the gross waste load of a meat packing plant.

Paunch material, high in total solids concentration, interferes with the efficient workings of traditional waste treatment methods. The pollution load caused by the edible rendering processes depends on which rendering process is used.

Wet rendering is the older method and is not being adopted by newer plants. If tank water is evaporated in the wet rendering process, waste loads can be reduced by 50%. Dry rendering and low temperature rendering, the newer methods, reduce waste loads by 60%.

In general, the more advanced the technology, the smaller the waste water and waste load per unit of product. The most common form of waste treatment facility in the meat products industry is the catch basin. This basin is really a sedimentation tank fitted with grease skimming equipment. Properly

designed, catch basins reduce waste loads by 25%. But existing catch basins are underdesigned from the point of view of pollution control, Interior points out.

Approximately 85% of the 219 plants have some form of waste treatment facility. In 1966 these industrial facilities reduced waste load volumes by one third. The cost to the entire industry was $35 million in investments in equipment and an additional $3.5 million for operation and maintenance of these facilities. Nevertheless, in 1966 approximately 75% of the waste water from the meatpacking industry was treated by municipal treatment facilities. The meat products industry paid $6 million for these services, but the treatment removed only 56% of its BOD, according to the profile.

Poultry processing

Three processes—blood recovery, screening of feathers, and cleanup—account for the bulk of the waste load from the poultry processing industry. Blood recovery can reduce waste loads by close to 38%. In 1966 only 56% of all the plants surveyed (poultry packers that killed 30% of all birds processed that year) recovered blood. Thus, the Interior profile notes, blood recovery is one step where the poultry processing industry could make a substantial pollution reduction.

Because feathers are not easily degradable by biological waste treatment, processing plants must use screens to remove feathers.

The most common method of waste

water treatment used by poultry processors is municipal treatment. The average plant and even those employing advanced levels of technology use a screening process to remove feathers and solids from the plant effluent. In 80% of the plants this screening is the only type of pretreatment employed by industry. All further treatment is done by the municipal treatment facility.

In 1966 the poultry processing industry spent $6 million in investments in equipment and an additional $1 million for operation and maintenance of these facilities. In the same year the industry spent a total of $5.6 million for treatment of its waste waters at municipal treatment facilities.

Dairies

The dairy industry comprises five major subdivisions for the manufacture of this industry's products—creamery butter, natural and processed cheese, condensed and evaporated milk, ice cream and frozen desserts, and fluid milk.

The profile for the dairy industry, based on data for year 1963, reveals that dairy wastes are similar in all five groups. The dairy industry's most significant source of water pollution is the loss of product in the various process streams of the industry. Because process improvement can lead to a considerable financial saving, the dairy industry has worked to reduce the wastes in process streams. In turn, the search for process improvement is a contributing factor in the move toward the consolidation and

construction of ever larger plants.

In addition to product loss, other significant dairy industry wastes include water, soap, and chemicals used in sanitation procedures; cooling water; skim milk and buttermilk from butter manufacture; and cream and whey from cheese manufacture.

Typically, large, technologically advanced plants have process stream wastes of 0.5%, compared with a typical plant which has a waste stream with 1–5% product, or a small plant of older technology with a 2.5% product waste stream.

In general, dairy wastes have a high BOD demand in relation to volume but are low in suspended solids. Most dairy plants are simply not large enough to justify the cost of an onsite treatment system. So, industry will continue to use municipal treatment facilities at an increasing percentage in the coming years.

Whey from cheese manufacture has no great commercial value, creates the largest sewerage BOD load, and remains a problem for today's dairy industry. Pretreatment of this industry waste is not required prior to discharge in municipal sewers. If the municipal sewer is inadequate in size, either pretreatment or prohibition of dumping is necessary.

Plastics materials and resins

The several processes involved from synthesis of the monomers to the fabrication of the completed plastic material were evaluated for the plastics materials and resins profile. In most

cases, the synthesis of the monomer produces considerably more waste than the production of the polymer from the monomer.

Accounting for more than 85% of all plastic production in the U.S. (14.25 billion pounds per year in 1968), nine subdivisions of plastic materials and resins—cellulosics, vinyls, styrenes, polyolefins, acrylics, polyesters and alkyds, urea and melamines, phenolics, and miscellaneous resins—generate 113 million pounds of five-day BOD. Water renovation systems removed 55% (62 million pounds) of BOD, but the remaining 45% (51 million pounds) goes to the water courses of this nation. Of these 51 million pounds of BOD waste, 18 million pounds pass largely unaffected through the treatment plant, and no effort is made to treat the other 33 million pounds.

By 1977 plastic production in the U.S. will probably reach 26 billion pounds annually. This product level will generate slightly more than 200 million pounds of BOD. Assuming a constant 55% removal, the waste load to water courses will nearly double in the next decade, increasing from 51 million pounds of BOD in 1967 to 90 million pounds of BOD in 1977.

Although BOD currently is the best measure available and is most representative of waste load, it simply does not give an adequate accounting of organic loading. Furthermore, as a production monitor, it is five days late. Since the waste water loading in the plastics materials and resins profile is based upon a test that was developed for sanitary waste, the BOD level is inadequate for chemical industrial waste.

Many renovation systems in current use will not meet the standards of the next decade. (Industrial wastes contain a small portion of readily biodegradable soluble organics with balanced nutrients.)

In 1967 plastics materials and resins industry spent $2.2 million to remove 62 million pounds of BOD. The breakdown includes $0.6 million sewer charges to manufacturers utilizing municipal facilities for water renovation, $0.3 million capital goods depreciation, and $1.3 million for operation and maintenance of industry treatment plants.

Only CHEMICAL ABSTRACTS
funnels the flow of
world wide chemical
and chemical
engineering
data your
way
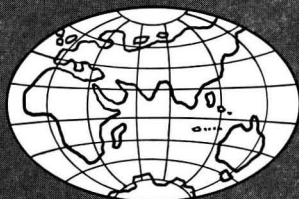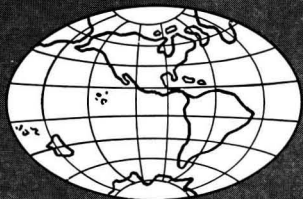
CHEMICAL ABSTRACTS is the only complete and comprehensive chemical abstracting service in the world which can provide you with data and ideas to keep your research, development, production or educational activities moving forward. It is compiled through the systematic collecting, analyzing, and processing of articles and papers from nearly 12,000 journals published in 100 countries and in more than 50 languages. Also processed are patents issued by 25 countries and irregular publications such as books, conference proceedings and government bulletins.

Issues are published each week and are indexed by subject, author, and patent number for fast, easy reference to specific areas of interest. Seven volume indexes are issued every six months providing you with the keys to the entire literature of chemistry.
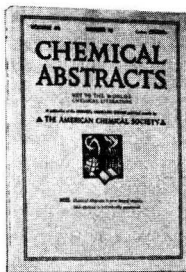
Through CHEMICAL ABSTRACTS you can keep on top of all information published anywhere on anything in the world of chemistry. Users consistently report significant savings in time, money and effort by avoiding duplication in research . . . capitalizing on the findings of others . . . learning about new methods and processes.

Act now to have CHEMICAL ABSTRACTS on your desk or in your library. Write for complete information and subscription prices to: E. G. Johnson, Subscriber Information Dept. CA.

CHEMICAL ABSTRACTS SERVICE
American Chemical Society
Columbus, Ohio 43216

Renovated Waste Water Creates Recreational Lake

In pilot studies aimed at converting a borrow pit to an aquatic park, the major hurdle proved to be the reduction of phosphorus to concentrations that limit algal growth

Lancaster, Calif., is a rural community of about 35,000 on the southern edge of the Mojave Desert about 80 miles northeast of Los Angeles. For more than 20 years the waste water of the area has been given primary treatment followed by biological stabilization in oxidation ponds. Presently, 3 million gallons per day are treated and then lost to the atmosphere by evaporation. With annual rainfall of only 2 to 3 inches, the area depends on underground sources for both irrigation and domestic water supplies. Supplemental water will eventually be imported from Northern California. In the interim, ground water must be conserved for domestic, industrial, and irrigational purposes. In recognizing the community's need for water-based recreational facilities, the Los Angeles County Engineer proposed converting an existing borrow pit to an aquatic park featuring three lakes with a combined surface area of 19 acres.

The Sanitation Districts of Los Angeles County joined with the Advanced Waste Treatment Branch of the Federal Water Pollution Control Administration, Department of the Interior (formerly the U.S. Public Health Service), in a research effort to investigate the best possible methods of renovating the oxidation pond water to a point where it would be suitable for use in the lakes. Since oxidation ponds are used in many arid areas, research groups hoped that techniques developed in Lancaster would be applicable to other localities.

The water in the oxidation ponds is unsuitable for use in the lakes without further treatment. The green algae which abound in the oxidation ponds supply oxygen to the bacteria which decompose the organic matter in the waste water. However, since algae receive their energy from light they photosynthesize and produce oxygen only during daylight hours. The water becomes supersaturated with dissolved oxygen with maximum concentrations as high as 40 milligrams per liter in Lancaster. The bacteria, however, utilize oxygen continuously and can reduce the dissolved oxygen of the water to as low as 1 mg./l. or less at night. Fish cannot survive in such an extreme environment, a fact confirmed by previous attempts to raise carp in the oxidation ponds.

In addition to sunlight, algae require carbon, nitrogen, phosphorus, and certain trace elements to live. The carbon is obtained from carbon dioxide and bicarbonate in the water, raising the pH to between 8.5 and 9.5, which is a difficult range for fish. Therefore, both the bacterial and algal populations in the oxidation pond water would have to be drastically reduced for the water to be suitable for use in recreational lakes. The bacterial population could be reduced by reducing its food supply—the organic matter and algae in the water. However, a new cycle of algae growth, organic matter production, and bacterial decomposition is sure to start unless one of the essential algal nutrients is also removed. The only essential nutrient that could readily be reduced to growth-limiting concentrations is phosphorus, and its removal has become a major objective of the study.

Research objectives

The immediate study objective was to determine and pilot the most economical method of renovating the waste water for use in the recreational lakes. However, the lack of recognized limiting quality criteria for recreational lake water required that arbitrary criteria be established as contingent objectives in evaluating processes. But these criteria were flexible and could be revised as the study revealed cost data, process capabilities, and what may be the special behavior of renovated water.

Reviews of studies by Sawyer (1947) and Malhatra (1964), consultation with algologists at the Robert A. Taft Sanitary Engineering Center, and knowledge of the recent experience of the Santee County Water District with recreational lakes supplied by soil-filtered waste water near San Diego (1966) provided the basis for the following initial quality objectives:

• Turbidity of less than 10 Jackson turbidity units (JTU).
• Phosphate concentration of less than 2 mg./l. as PO_4.
• pH of less than 8.0.
• Low concentration of chemical oxygen demand (COD) and biological oxygen demand (BOD).
• Algae counts less than 10,000 per milliliter.
• Coliform and virus determinations to meet requirements of the County Health Officer.

Subsequent experience has resulted in the revision of the phosphate objective from 2 mg./l. to 0.5 mg./l. or less. The other criteria are still considered adequate. Product water, or water produced by the selected process, is generally of better quality than would be indicated by these objectives. The turbidity objective of 10 JTU, for example, is double the average turbidity of the product water. The final turbidity is a consequence of the chemical dosage required for phosphate removal. The low turbidity makes the water clear and sparkling, which will increase its public acceptance as it enters the lake.

Oxidation pond facilities

The District 14 Water Renovation Plant features primary sedimentation followed by 240 acres of oxidation ponds. (Figure 1 shows the project site, facilities, and oxidation pond flow pattern.) Each of the eight ponds has a surface area of about 30 acres and 5- to 7-

FEATURE

Franklin D. Dryden, Los Angeles County Sanitation Districts, Los Angeles, Calif. 90057
Gerald Stern, Southern California Field Station, FWPCA, Garden Grove, Calif. 92640

foot water depth. Only the first four ponds are in the treatment series; the last four are used for winter storage when evaporation rates are low and are dried out in the summer to inhibit midge propagation.

Primary effluent is divided equally between Ponds 1 and 2 and dispersed through 400-foot diffusers to avoid overloading a portion of the pond. Pond 1 discharges into Pond 2; the combined flow then passes sequentially through Ponds 4, 3, and 5 as shown. The flow pattern can be varied as desired. The average residence time to the discharge of Pond 3 is between 45 and 60 days. Pond 3 is the designated source for water to be used in the recreational lakes and was the source for all water treatment studies conducted in this project.

The project was conducted in two phases:

• Determining the most effective and economical process for renovation of the waste water (Phase I).

• Operating the chosen process and evaluating the product water in simulated recreational lakes (Phase II).

Phase I studies

To accomplish the desired objectives in minimum time, three research steps that would normally be conducted successively were performed concurrently. They are:

• Collection of basic data on the character of the water to be treated.

• Laboratory jar test evaluations of various coagulants to determine the most feasible chemical treatment and the optimum conditions for removing algae, other suspended material, and nutrients.

• Pilot-plant process evaluation of promising processes to develop cost and performance data in order to select preferred processes for renovating the waste water.

Analyses of the plant primary effluent
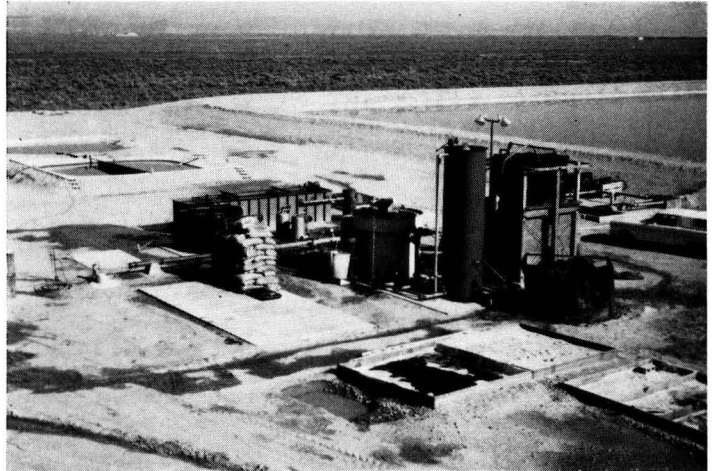
Pilot plant. *Six processes for water reuse were evaluated at Lancaster, Calif.*

Flow patterns are shown by arrows   1 inch equals 500 feet

Figure 1

Oxidation ponds and study area

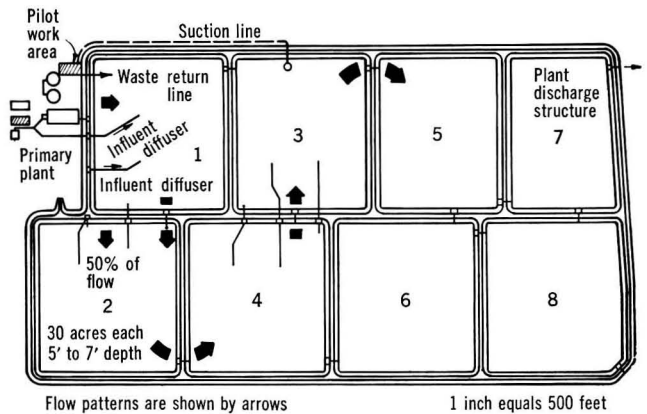and of the oxidation pond water began in October 1963. Grab samples were collected from the pond and analyzed for selected chemicals and algae genera and numbers. An automatic sampler was installed on the primary effluent in July 1964, to obtain more representative data. The average characteristics of the primary effluent are:

pH	7.2
Total alkalinity	258 mg./l.
Phosphate	45 mg./l.
Ammonia–nitrogen	27 mg./l.
COD	392 mg./l.
Suspended solids	90 mg./l.
Dissolved solids	553 mg./l.
Organic nitrogen	11 mg./l.
Nitrate–nitrogen	0.1 mg./l.
Nitrite–nitrogen	<0.01 mg./l.
Hardness	77 mg./l.
Calcium	32 mg./l.
Magnesium	3 mg./l.
Sulfate	70 mg./l.

Pondwide sampling established that the long detention times within the ponds and frequent strong winds resulted in excellent mixing and averaging of most chemical constituents at any given time.

In the course of the study we observed that, to achieve equivalent results, greater chemical doses were required during the winter and spring period of high total alkalinity, phosphate, and ammonia than during the summer and fall period when lower values prevailed. Essentially all chemical changes in Pond 3 were traced to either physical factors such as sunlight intensity, temperature, and wind mixing, or biological factors such as specie composition of the biomass, metabolic rates of the algae and bacteria, and growth of crustaceans.

Ammonia concentration showed a cyclic pattern—less than 3 mg./l. during the summer and fall, increasing to about 20 mg./l. for much of the winter and spring (Figure 2). The seasonal decrease of ammonia by biological synthesis represents most of the nitrogen removal that is accomplished in the oxidation ponds. The low ammonia levels in the summer correlate with the period of rapid metabolism. The high levels in the winter correspond to the period when low sunlight intensity and low temperatures reduce the rate of photosynthesis. Nitrate and nitrite concentrations are generally low throughout the year. However, in the spring of 1966 as temperatures were rising, nitrite

values reached 10 mg./l. for about a week before the development of nitrate-producing bacteria, which converted some of the nitrite to nitrate. Denitrification may also have occurred; nitrate values never exceeded 2 mg./l., while the nitrite dropped almost to zero. Organic nitrogen has been observed as high as 20 mg./l., coinciding with high algal counts.

Ammonia variations are also accompanied by similar changes in total alkalinity, which averages 260 mg./l. in the winter and spring and 220 mg./l. in the summer and fall. The higher alkalinity and ammonia concentrations, which tend to buffer pH changes, and the lower temperature, which reduces chemical reaction rates, require that additional coagulants be used for equivalent treatment.

Total phosphates

The total phosphate concentration is also higher during the winter and spring than in the summer and fall period. Biological synthesis, sedimentation of algae, and possibly calcium phosphate precipitation at the higher pH values of the summer and fall all contribute to lowering total phosphate levels. The low total phosphate concentrations permit low coagulant dosages for equivalent residuals.

Other periodic variations between the colder and warmer seasons which are important to the tertiary process include:

• Temperature, which varies from 6° to 30° C.
• pH, which ranges from 7.5 to 9.6.
• Chemical oxygen demand, which decreases from 300 to approximately 200 mg./l.
• Biological oxygen demand, which decreases from 50 to 40 mg./l.
• Suspended solids, which decrease from 100 to 75 mg./l.
• Dissolved solids, which decrease from 640 to 570 mg./l.
• Turbidity, which ranges from 90 to 170 JTU in the cold season and from 40 to 150 JTU in the warm season.

Algae genera and predators

The oxidation ponds contain about 66 algae genera in varying concentrations (50,000 to 700,000 counts per ml.) throughout the year. *Scenedesmus* is the most common, although *Euglena*,

Ankistrodesmus, Phacus, Oöcystis, Chlorella, and *Nitzschia* have also been dominant.

The most common crustaceans found at random in the oxidation ponds at different times are *Daphnia* and *Cyclops.* These algae predators contribute to the variation in algae counts and algae genera.

The oxidation ponds are very effective in reducing both bacteria and virus levels. The bacteria reductions, after 45 to 60 days' detention, were more than 99.7% (Figure 3). Viruses were detected in 96% of primary effluent samples, and in only 8% of the Pond 3 samples. Polioviruses I, II, and III, the adeno group, coxsackievirus B-3, echovirus 7, and reovirus have been identified in the primary effluents. In oxidation Pond 3 waste water, one sample contained polio II and three samples contained an unidentified virus.

Laboratory studies

Laboratory studies included jar test evaluation of coagulants. The object was to determine the most effective coagulants and coagulant aids, their required dosages, the best flocculating conditions, and relative costs.

The jar test apparatus consisted of a 10-place stirrer equipped with a variable speed paddle drive. All tests were performed on water from oxidation Pond 3 following the procedures suggested by Cohen (1957).

To facilitate screening a maximum number of samples, the effectiveness was rapidly estimated by a turbidity measurement. Additional chemical analyses were performed on particularly promising samples.

The coagulant combinations tested are too numerous to report. The major coagulants were:

• Aluminum sulfate $[Al_2(SO_4) \cdot 14H_2O]$ as a commercial grade alum, with and without pH adjustments and other coagulant aids.
• Calcium hydroxide $[Ca(OH)_2]$ as lime, both high-calcium $[90\% \ Ca(OH)_2]$ and the less expensive dolomite $[58\% \ Ca(OH)_2$ and $41\% \ Mg(OH)_2]$.
• Ferric sulfate $[Fe_2(SO_4)_3]$, 70% pure, 30% inert.
• Dow C-31 cationic polyelectrolyte. (Dow NC1118, UCAR-149, and Nalco 600 cationic polyelectrolytes were also tested. Dow C-31 test results were very

similar to the other three cationic poly-electrolytes.)

• Sulfuric acid (H_2SO_4) at 66° Baumé.

Jar test studies were run to determine costs for the primary coagulants (Figure 4). Dolomitic lime was used in the cost analyses even though high-calcium lime was actually used in pilot studies because it was easier to handle. The jar test showed the two products to be equally effective at equivalent dosages. Ferric sulfate was omitted from further primary coagulant studies due to its higher cost.

The majority of the jar tests were conducted with alum, lime, and various cationic polyelectrolytes as coagulants. In addition, sulfuric acid and carbon dioxide were used for pH adjustment in conjunction with alum coagulation.

Coagulant studies

Tests were also run for primary coagulants and coagulant combinations (Figure 5), including the overall effect of levels of chemical constituents in Pond 3, to determine their cost.

Figure 6 shows the effectiveness and costs of coagulant combinations during periods when the difference in chemical requirements is related to changes in the characteristics of Pond 3 water. Lime was less effective than alum in the spring period, although it was competitive with alum in the fall. As for total phosphate removal, alum coagulation was much more successful than lime, in the colder season, for reducing phosphate concentrations (Figure 7). With lime coagulation, a substantial colloidal precipitate remained, which could account for the higher phosphate residual.

The use of cationic polyelectrolytes or acid for pH adjustments materially reduced the quantities of alum required to accomplish turbidity objectives in each seasonal period, although the coagulant cost in the spring was much higher than in the fall. However, cationic polyelectrolytes and sulfuric acid do not remove soluble phosphate. Consequently, alum in combination with acid or polyelectrolytes is not as effective in removing phosphate so the larger dosage of alum alone. Since alum was the most effective coagulant, it received the most attention in pilot work.

Jar test studies were also used to determine optimum conditions for successful alum coagulation of Pond 3

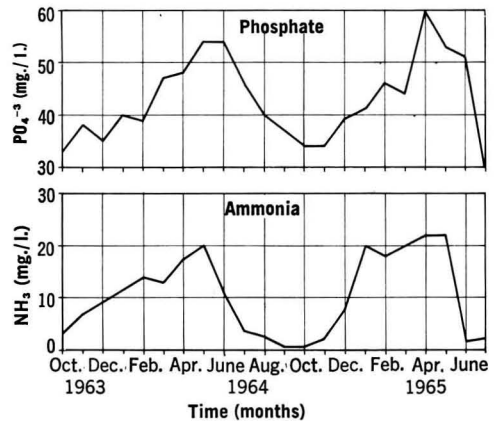**Figure 2**

Phosphate and ammonia concentrations in Pond 3

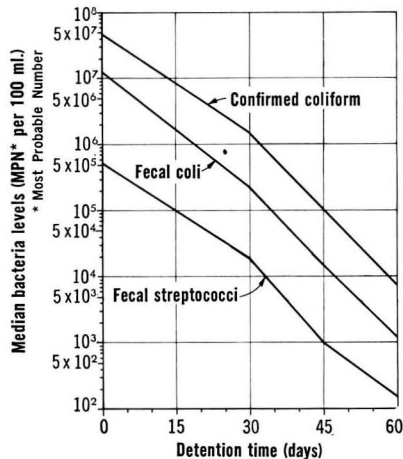

Figure 3

Median bacteria counts through oxidation ponds

Figure 4

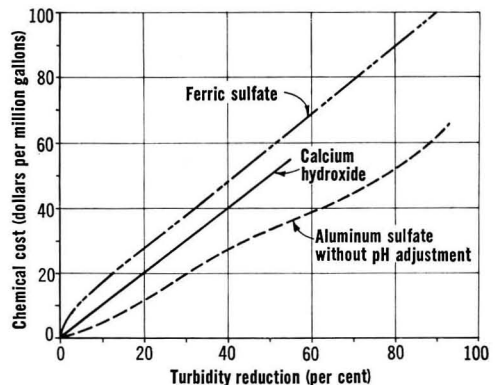**Cost vs. removal efficiency for primary coagulants based on jar tests**
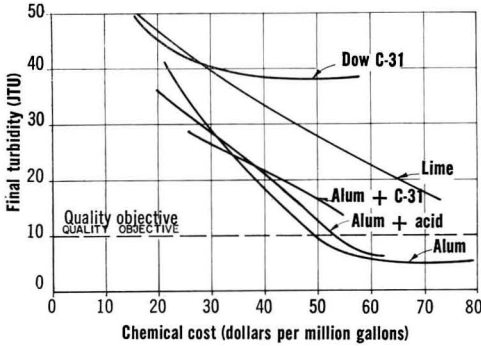
Final turbidity (JTU)

Dow C-31

Lime
Alum + C-31
Alum + acid
Alum

Quality objective

QUALITY OBJECTIVE

Chemical cost (dollars per million gallons)

Final turbidity (JTU)

Dow C-31

Alum

Quality objective

Lime

Alum + Dow C-31

Residual turbidity (JTU)

Lime

Alum + acid

Alum + Dow C-31

Quality objective

Alum

Chemical cost (dollars per million gallons)
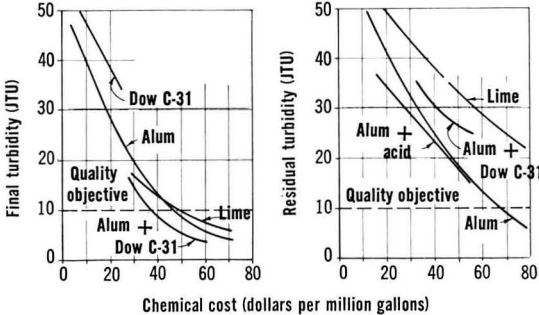
Low alkalinity and nutrient period
Alkalinity 220 mg./l.
Phosphate 35 mg./l.
Ammonia nitrogen 2 mg./l.

High alkalinity and nutrient period
Alkalinity 260 mg./l.
Phosphate 55 mg./l.
Ammonia nitrogen 20 mg./l.

Residual phosphate (mg./l.)

Cost basis
Alum: $48.40 per ton
Lime: $20.00 per ton

Pond 3 water characteristics
pH 8.3
Turbidity 8.8 JTU
Alkalinity 260.0 mg./l.

Lime
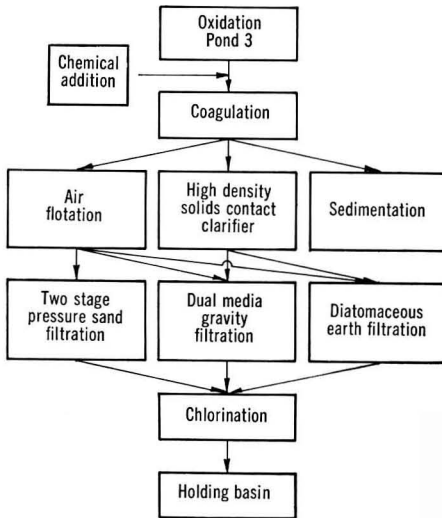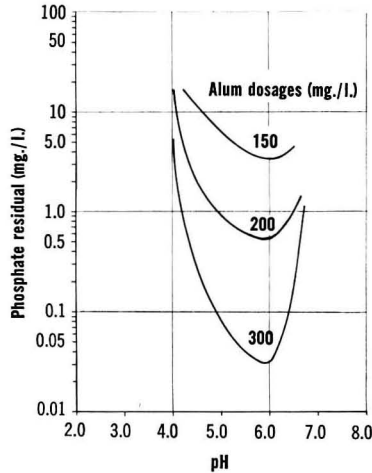
Alum

Chemical cost (dollars per million gallons)
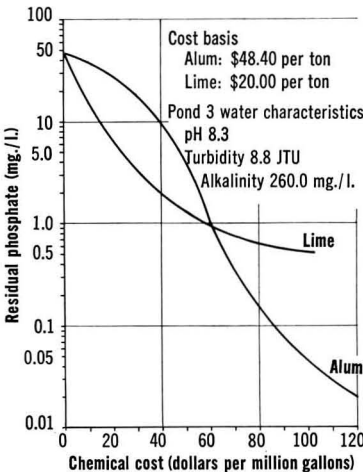
water for phosphate removal. These studies showed that with or without the addition of acid and base to change the initial pH and alkalinity, phosphate residuals were minimum when the final pH was approximately 6.0 (Figure 8). Increasing the alum dosage from 150 to 300 mg./l. also decreased the minimum phosphate residual. Others have found that the equilibrium constant for alum indicated phosphate can be removed to 0.04 mg./l. and that the pH for optimum removal is close to 6.0.

Pilot plant studies

The pilot plant studies were designed to evaluate and compare various treatment processes and to obtain reasonable cost estimates. The pilot area was arranged around a central run of influent and effluent piping with connections for six concurrent processes. Oxidation pond water was delivered to the pilot area from mid-depth on the north side of Pond 3 through a 1600-foot, 6-inch-diameter pipeline, and waste and product water were pumped back into Pond 1. Pilot units ranged in capacity from 1 to 50 gallons per minute (g.p.m.).

Initially, experiments were conducted to remove algae separately from the dissolved nutrients in the hope of producing a marketable algae for use as a poultry feed. A small microstrainer (23-micron screen), a pressure sand filter, and three types of diatomaceous earth filters were tested. These processes failed to produce the desired results. Removals with the microstrainer were totally inadequate and blinding by the bodies of crustacea and other foreign material occurred quite rapidly. The pressure sand filter removed a good percentage of the algae but not enough to be economical. Diatomaceous earth was quite successful in removing the algae, although color and turbidity of the product water were still high. The estimated value of the recovered algae was $25 per million gallons (based on $100 per ton), but the process costs for short filter cycles, separating the algae from the cake, and drying them, far exceeded the product value. More recent evaluations by Dr. William Oswald (University of California, Berke-

**Phosphate
residual vs. pH
based on
jar tests**

Figure 8 graph: Phosphate residual (mg./l.) vs. pH. Alum dosages (mg./l.) shown as curves labeled 150, 200, 300.

Pilot plant flow sheet (phase I)

Figure 9

ley) have shown some algae to be a substitute for fish meal, value per ton: $200.

Thereafter, the study concentrated on the best possible processes for clarifying the water. In spite of the potential savings to be gained by completely removing turbidity and dissolved nutrients in a single process, preliminary pilot work indicated that a combination of processes would be required to achieve the desired quality objectives. The first process would materially reduce suspended matter and nutrients by chemical treatment, and the water would be polished by filtration and disinfected by chlorination (Figure 9).

Chemical processes

Initially, the quality objectives for the chemical processes were a turbidity of 20 JTU or less and total phosphate concentration of less than 2 mg./l. Subsequent algal regrowth studies emphasized the need to reduce total phosphate levels to less than 0.5 mg./l. by using larger dosages of alum, which also reduced turbidity levels to the 5- to 10-JTU range. Turbidity was used to compare the relative effectiveness of the pilot processes in screening tests because of the ease and rapidity of measurement. The following types of pilot equipment were tested:

Portable water treatment plant. A completely self-contained trailer-mounted water purification unit of 25-g.p.m. rated capacity loaned to the project by the U.S. Army. It featured an upflow clarifier with a central mixing and flocculating chamber. Results were not satisfactory because of the release of supersaturated dissolved oxygen and other gases which buoyed the floc to the surface.

High density solids contact clarifier. A complete lime-coagulation and recarbonation water treatment unit of 25-g.p.m. capacity with provision for sludge recycle and auxiliary chemical addition. The first of two 10-foot high, 4-foot diameter vertical columns contains rapid mix, coagulation, and flocculation zones near the top with upflow clarifier and sludge collection zones in the bottom. The second column or recarbonator contains inverted trays
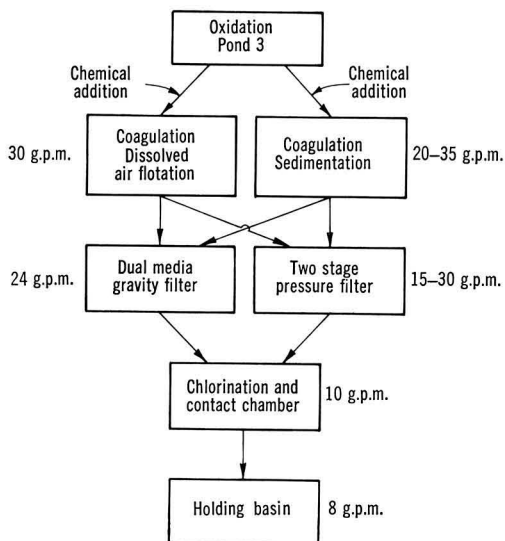
Continuous pilot plant flow sheet (phase II)

Figure 10

Figure 11

Residual turbidity vs. aluminum sulfate prior to filtration (pilot plant)
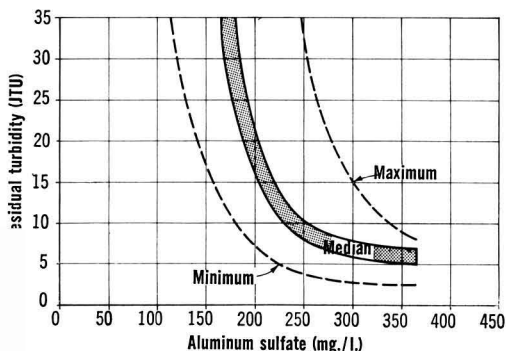
to adjust pH by adding CO_2 and a chamber for supplementary settling and sludge recycle. The unit did not operate successfully at its rated capacity but was adequate at 10 to 15 g.p.m.

Dissolved air flotation units. Pilot units in two sizes were used in this study:

• A 1-square foot air flotation unit—rated capacity 0.3 to 3.0 g.p.m., air dissolved into auxiliary water stream at 60 to 70 pounds per square inch (p.s.i.), manually skimmed, operated at about 1 g.p.m.

• A 6-foot diameter, 27-square foot × 6-foot deep air flotation unit rated at 50 g.p.m. Coagulated water entered a supersaturated mixing chamber in the center of the 6-foot high tank. Air dissolved into the recycle water is released in small bubbles that lift the floc to the top where it is skimmed into a trough. The clarified water flows to the bottom of the tank and up to and over a circular weir around its periphery. The unit was operated at flow rates between 20 and 50 g.p.m. with most runs at 30 or 40 g.p.m. The recycle stream was varied from 10 to 25 g.p.m. at pressures of 40 and 20 p.s.i., respectively. Air at about 15 cubic feet per hour was introduced by eduction into the suction of the recycle pump.

Sedimentation tank. A 1200-gallon circular tank, 4 feet deep and 7.5 feet in diameter, was baffled to serve for a brief trial of horizontal-flow sedimentation. At 11 g.p.m. there was a 2-hour detention time and an overflow rate of 340 gallons per day (g.p.d.) per square foot. A submerged discharge protected the effluent from floating algae. It was sufficiently effective to justify construction of a larger unit.

The high density solids contact clarifier, air flotation, and sedimentation processes were technically feasible. The sedimentation tank test results were almost identical to those obtained in the air flotation unit in contrast to the very poor results obtained in the truck-mounted upflow clarifier used in the early part of the study. The pilot-plant tests substantiated the jar tests results in that alum remained the most effective chemical coagulant. Thus, both air flotation and horizontal sedimentation with alum as primary coagulant were

chosen as the preferred processes to be evaluated in Phase II.

Filtration equipment. Polishing of primary process effluent by filtration provides a safety factor and produces a water of such clarity that its appearance will be pleasing to the public. Both diatomaceous earth filters and sand filters were tested. Diatomaceous earth filters were the following types:

• A low pressure reversible cake diatomaceous earth filter of 0.5 to 3 g.p.m., operated at approximately 1 g.p.m. for pilot tests.

• A truck-mounted 25-square foot pressure filter.

• A wound-wire pressure filter.

• A vertical leaf swimming pool pressure filter.

• A 1-square foot bench-scale pressure filter.

• A 50-square foot tube and shell pressure filter.

Sand filters tested were:

• A two-stage pressure sand filter of 2-foot depth and 2.2-square foot surface area per stage.

• Six 3½-inch-diameter, 0.06-square foot lucite gravity sand and dual media filter columns.

• A 12-square foot gravity sand or dual media (anthrafilt-sand) filter.

Diatomaceous earth filter effluents were consistently better than effluents from the dual media or pressure sand filters. However, diatomaceous earth filter cycles did not exceed 3 hours, resulting in excessive diatomaceous earth usage and high costs (estimated between $80 and $200 per million gallons). The short filter cycles were caused by blinding of the filter by algae and other particulate matter not removed in the previous separation process. The compressibility of the gelatinous floc contributed to the rapid blinding in spite of diatomaceous earth body feed rates of up to 90 mg./l. and influent water turbidities as low as 3 JTU.

Pressure sand and dual media filtration both reduced influent turbidities by 25 to 50% resulting in filter effluents with turbidities of 10 JTU or less when the effluent turbidity from the chemical process was between 10 and 20 JTU. Longer operating cycles and the reuse of

the filter media provided a substantial cost advantage for sand and dual media filter over the diatomaceous earth units.

Preferred processes

The combined processes to accomplish the quality objectives at lowest cost were:

• Alum coagulation.

• Either dissolved air flotation or plain sedimentation.

• Either pressure sand or dual media gravity filtration.

• Chlorination.

These combined processes were arranged in combinations and automated sufficiently to permit their 24-hour per day operation while being attended only 8 hours per day (Figure 10). The processes were operated for a full year with the product water being monitored and fed to a small simulated lake to demonstrate the continuous production of high quality water, to compare the alternative chemical treatment and filtration processes for reliability at all times of the year, and to evaluate the behavior of the product water in the simulated lake.

The horizontal flow sedimentation unit was designed for 20 to 50 g.p.m. at overflow rates between 300 and 700 g.p.d. per square foot. The effluent was removed by a submerged launder to avoid floc that might float to the surface. This feature was found to be unnecessary since there was almost no floating floc in a year of operation. A mechanical scraper removed the settled sludge.

Although there was almost no differ-

ence in quality characteristics during a year of comparative operation, the sedimentation and dual media gravity filtration systems were selected over the flotation and pressure sand filter systems on the subjective basis of simplicity of operation and general reliability. Alum dosages were increased to 300 mg./l. during the evaluation study to reduce phosphate to its lowest practical minimum. As later tests established, algae growth is not noticeably inhibited at phosphate concentrations above 0.5 mg./l.

Residual turbidity as a function of aluminum sulfate dosage for pilot plant air flotation and horizontal sedimentation tests was averaged over the Phase I and Phase II study (Figure 11). Also, residual phosphate was plotted as a function of alum dosage for pilot plant tests conducted in the Phase I and Phase II study, and averaged for the high alkalinity–high phosphate and low alkalinity–low phosphate periods (Figure 12). These studies show the effectiveness of increasing the alum dosage to 300 mg./l. or more to meet both the turbidity and total phosphate quality criteria for the recreational lake water.

Final selection of processes

The process chosen for converting the oxidation pond water for use in recreational lakes features:

• Coagulation with approximately 300 mg./l. of commercial grade aluminum sulfate and 20 minutes of floc-

Figure 12

Residual phosphate vs. aluminum sulfate prior to filtration (pilot plant)
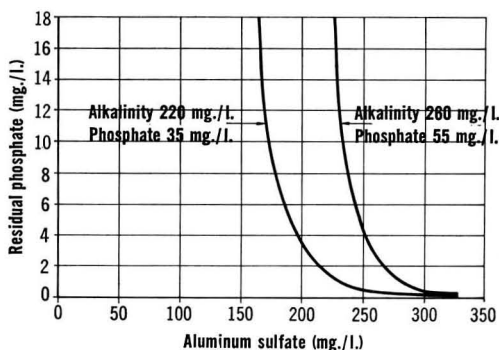
culation with a typical water treatment plant paddle flocculator.

• Sedimentation with an overflow rate of about 400 g.p.d. per square foot in a horizontal flow tank equipped with sludge scrapers. The sedimentation tank will be covered to prevent wind-generated currents and turbulence.

• Filtration through a dual media gravity filter comprised of 18 inches of 0.5-mm. anthracite over 8 inches of Number 20 sand.

• Chlorination at about 6 to 15 mg./l. Chlorine may be added prior to the sedimentation tank (to reduce crustacean populations reaching the filter) or after the filtration step.

• Minimum 8-hour retention in a chlorine contact chamber.

• Skimmings and sludge from the sedimentation tank and backwash water from the filter will be returned to the inlet of the plant. Most solids will be removed with the primary sludge and digested.

The characteristics of the processed water are compared with those of Pond 3 in Table 1.

A 500,000-g.p.d. facility is being designed to supply the 19-acre recreational lakes. This added supply will prevent dissolved solids in the lake from increasing beyond 700 mg./l. due to evaporation. The water will also be used to irrigate the surrounding park. The capital cost of the plant is estimated at about $150,000. Operating costs are estimated at $184 per million gallons, chemical costs accounting for $70 per million gallons. When expanded to 3-million gallons per day (m.g.d.) capacity, the total cost of capital, operation, and maintenance is estimated at about $150 per million gallons compared to about $200 per million gallons for imported water.

Holding basin studies

Holding basins were constructed to simulate the recreational lake environment. The objectives were evaluation of the process water quality criteria, determination of the chemical and biological behavior of the water, determination of the tolerance of fish for the water, and testing of controlling auxiliary methods of algal regrowth. Selected laboratory tests were also conducted on processed water to determine the relationship between phosphate concentration and algae regrowth.

Three different basins were used:

several 1200-gallon, 7.5-foot diameter, 4-foot deep rubber tanks; two 10,000 gallon, 4-foot maximum depth concrete-lined ponds; and an unlined 250,000-gallon, 10-foot deep simulated lake.

During the initial stages of the pilot program, several batch test evaluations of the treated water were conducted in 1200-gallon rubber tanks. Alum and lime were used in several concentrations such that the product water contained between 1 and 5 mg./l. phosphate. Extensive regrowth occurred in each case within two months. Concentrations of *Chlorella* and *Ankistrodesmus* reached 600,000 cells/ml.

In another experiment, phosphate was reduced to 0.2 mg./l. with 300 mg./l. of alum, and the water divided between two 1200-gallon tanks. Dipotassium phosphate was added to one tank to raise the phosphate concentration to 56 mg./l. Regrowth of algae was greatly retarded in the low phosphate water although, after six weeks, both test basins had similar cell counts, turbidity, and appearance.

The high phosphate water produced a great deal more algae in the same time period and accumulated a significant sludge deposit of dead algae on the tank bottom. This test indicated that phosphate reduction would not necessarily influence the actual concentrations of algae to be expected in the recreational lakes but that rates of algae production would be significantly inhibited. As a consequence there should be fewer maintenance problems in the lake due to sludge accumulations and the lake environment should be more suitable for fish.

Draw and fill tests

A long-term experiment consisted of adding alum-treated water with low turbidity and phosphate to the 10,000-gallon pond to maintain about a 40-day detention period. All of the water was filtered and some of it chlorinated. Alum doses varied between 200 and 300 mg./l. (Eight months' data are averaged in Table 2 for the period between November 1964 and June 1965.) Generally pH values, which were between 6.5 and 7.5 for the treated water entering the basin, rose to pH 9 and phosphate was within the 2 mg./l. maximum phosphate quality criterion initially set. The pH rise probably resulted from algae fixing CO_2 and HCO_3

from the water. The water also contained COD and algae concentrations similar to or greater than Pond 3. The dissolved oxygen concentration never reached the intolerably low values observed in Pond 3.

Several other proposed methods of controlling algae regrowth were tested. Lampblack and powdered activated carbon were used without success. In theory, the carbon would adsorb sunlight and prevent light penetration to the algae. However, the carbon failed to stay suspended in the water for more than a few days and no growth inhibition was noticed.

Crustaceans were placed in the water and on two occasions, when the pH was lowered with acid to pH 7, blooms of rotifers and crustaceans consumed nearly all the algae. However, the crustaceans died and algae growth eventually resumed. Chlorination up to 10 mg./l. is not effective in reducing algae concentrations for more than a few days. Organic algicides and copper compounds controlled certain algae species but they were not effective for all types of algae. Furthermore, they are not effective for any significant time when used at concentrations that would not be harmful to fish.

All of these studies were conducted during the pilot process evaluations when it was still uncertain whether phosphate control could be used to prevent objectional algae growths in the recreational lakes.

Pilot plant operation

In July 1965, the pilot plant began operating continuously and at higher alum dosages. (Chemical data for the 10,000-gallon concrete-lined basin are summarized in Table 2 for the period between September 1965 and April 1966.) Use of 300 mg./l. of alum reduced phosphate residuals to one fifth and algae counts to between one third and one fourth. The predominant algae genera at times changed from the typical green algae usually associated with polluted water (*Scenedesmus*, *Closteridium*, and the like) to *Nannochloris coccoides Naumann*, very small green algae that have rarely, if ever, been observed in polluted water.

The effect of low phosphate residuals was even more striking in the 250,000 gallon unlined basin (chemical and algae data are shown in Table 2). *Nannochloris coccoides Naumann* was the most

prominent and often the only algae genus observed. Because of the extremely small size of *Nannochloris coccoides*, algae counts in the basin did not equal the weight of organic matter in oxidation Pond 3, which averaged about 200,000 counts/ml. The dissolved oxygen levels in this and the smaller 10,000-gallon basin were at least 5 mg./l. or more throughout a year of operation, and the diurnal dissolved oxygen changes were minor compared to those in Pond 3.

Algae will strip most of the remaining orthophosphate from tertiary effluent. Total phosphate concentrations entering the basins averaged 0.25 to 0.3 mg./l., but concentrations in the lakes stayed below 0.05 mg./l. Algae used the phosphate, then settled to the bottom where the phosphate was unavailable. However, extensive decomposition of the sludge layer might cause a sharp increase in phosphate concentration. Low phosphate concentrations (<0.5 mg./l.) limited growth in both holding basins during the continuous pilot plant preferred process studies in which approximately 300 mg./l. alum was used.

Laboratory studies were also conducted to determine if the reduction in phosphate in the pilot plant was in fact inhibiting algae growth. Samples of product water were injected with varying concentrations of phosphate and of other micronutrients (usually Hutner's micronutrient solutions[a]) known to be essential for algae growth. The samples were exposed to continuous fluorescent lighting and stirred with a wrist-action shaker. The tests showed that:

• Some algae growth occurred at phosphate concentrations as low as 0.05 mg./l.

• Phosphate concentrations of 0.1 to 0.3 mg./l. significantly inhibited the rate and density of algae growth.

• Phosphate concentrations below 0.5 mg./l. inhibited algae growth.

• Phosphate concentrations between 1 and 30 mg./l. supported about the same amount of algae growth.

To inhibit algae growth entirely would probably require removal of phosphate to concentrations well below

[a] Hutner's micronutrient solution: The complete solution added 0.76 mg./l. zinc, 0.2 mg./l. boron, 0.14 mg./l. manganese, 0.03 mg./l. iron, 0.04 mg./l. copper, 0.06 mg./l. molybdenum, and 1.75 mg./l. EDTA (ethylenediaminetetraacetic acid). Other solutions with one or more nutrients left out were also used.

TABLE 1

Comparison of Pond 3 and processed water characteristics

Characteristics	Pond 3 water	Product water
pH	8.3	6.7
Turbidity (JTU)	90	4
Total alkalinity (mg./l. as CaCO₃)	260	95
Hardness (mg./l. as CaCO₃)	80	100
Suspended solids (mg./l.)	75	6
Dissolved solids (mg./l.)	575	575
Chemical oxygen demand (mg./l.)	250	50
Biological oxygen demand (mg./l.)	38	<10
Dissolved oxygen (mg./l.)	0.1–40	7–15
Ammonia–N (mg./l.)	0.1–20	0.1–20
Organic–N (mg./l.)	7–20	1–3
Nitrate–N (mg./l.)	1–4	1–4
Nitrite–N (mg./l.)	0.1–12	0.1–12
Total nitrogen (mg./l.)	7–20	3–20
ABS (mg./l.)	3	3
Phosphate (mg./l.)	40	0.25
Algae (counts/ml.)	200,000	7,000
Confirmed coliform (MPN/100 ml.)	7,900	<1.8
Chlorine residual (mg./l.)	—	0.2–0.5
Sulfate (mg./l.)	60	240

TABLE 2

Comparison of water characteristics in holding basins

Observation period	Water temperature (° C.)	pH	Phosphate (mg./l.)	Algae counts (thousands per ml.)	Predominant algae genera
10,000-gallon holding basin					
Pilot plant process evaluation Nov. 1964–June 1965	11	9.0	0.73	926	Closteridium and Scenedesmus
Continuous pilot plant evaluation Sept. 1965–Apr. 1966	13	8.9	0.12	247	Oscillatoria, Scenedesmus, Nitzschia, and Nannochloris coccoides
250,000-gallon holding basin Sept. 1965–Apr. 1966	15	8.8	<0.05	~2400	Nannochloris coccoides

0.05 mg./l. in the product water. Such removal is economically unfeasible and appears unnecessary because of the apparent suitability of the treated water for the recreational lakes.

Fish survival tests

Approximately 125 game fish (25 bass, 50 bluegill, and 50 catfish) were placed in the 10,000-gallon and 250,000-gallon basins for observation. Some 700 Gambusia or mosquito fish and 20 fathead minnows were also added to

provide food for the larger game fish. About 90% of the fish are still active in the ponds. A few fish were lost on four different occasions because of specific, but unrelated, causes.

Several fish died when the chlorine residual increased from 0.2 to 1.5 mg./l. in the 250,000-gallon basin. Rising ammonia concentrations in December had eliminated free chlorine residuals and the dosage was increased to 12 to 15 mg./l. to maintain bactericidal control with the less effective

Franklin D. Dryden *is deputy assistant Chief Engineer for Sewerage of the Sanitation Districts of Los Angeles County, a position he has held since November 1966. Previously (1963–66), he was Division Engineer for Research and Development. Altogether, Mr. Dryden has been with the Sanitation Districts for 10 years, having worked briefly for the State of California Bureau of Sanitary Engineering before his military service. Mr. Dryden received his B.S. (1954) in engineering and his M.S. (1957) in civil engineering from California Institute of Technology. He is a member of the American Society of Civil Engineers (Sanitary Group) and the Water Pollution Control Federation, and he is a registered professional engineer in the State of California.*

Gerald Stern *is Chemical Engineer and Project Officer, Process Analysis Section, Southern California Field Station, Federal Water Pollution Control Administration, U.S. Department of the Interior, a position he has held since 1962. Previously (1961), he worked for American Potash and Chemical Corp. and (1960–61) Knolls Atomic Power Laboratory–General Electric Corp. Mr. Stern has also been with Goodyear Atomic Corp. (1956–59). He received his B.S. (1955) in chemical engineering from New York University, and has taken graduate courses in chemical engineering, nuclear engineering, and nuclear chemistry at Ohio State University, Rensselaer Polytechnic Institute, and the University of Cincinnati. Mr. Stern is a member of ACS, the Water Pollution Control Federation, and the California Water Pollution Control Association.*

chloramines. The chloramines were so stable, however, that they were not utilized by other organics in the large holding basin. Reduction of the chlorine dose resulted in recovery of the remaining fish.

Again during the colder season, another effect of high ammonia concentrations was observed when the ammonia reached 8 mg./l. and the fish began to exhibit signs of distress. The high ammonia concentration coincided with a rise in pH apparently related to increased algal activity as water temperatures were also climbing.

At higher pH values, the percentage of ammonia in the form of ammonium hydroxide increases substantially and apparently becomes a toxic agent to fish. This problem can be circumvented in the proposed 0.5-m.g.d. tertiary treatment plant by selective storage and withdrawal of water low in ammonia. The ammonia entering the oxidation ponds is readily converted to other nitrogen compounds during periods of warm weather. With an average detention time of 45 to 60 days between the inlet of the oxidation ponds and the point of withdrawal to the tertiary process, ammonia levels do not rise substantially in Pond 3 until some time around December. By April, rising water temperatures cause a sudden drop in ammonia concentrations throughout the oxidation ponds. By filling oxidation Pond 3 to capacity prior to the rise in ammonia concentrations and then bypassing around it during the winter, there will be low ammonia content water for the recreational lakes throughout the year.

During the latter part of the cold season in 1966, the dissolved oxygen level fell below 3.5 mg./l. throughout the 250,000-gallon simulated lake. The water had a brownish appearance and algae counts decreased to 50,000 cells/ml. Some fish were in distress. Artificial aeration was provided and the dissolved oxygen level increased to saturation within three days. The brownish color was probably caused by a bacterial bloom that used up more oxygen than was being produced by the few algae present.

This experience emphasized that any biological system is subject to unpredictable changes and that blooms of bacteria, crustaceans, or algae may result in occasional oxygen depletion in any recreational lake using reclaimed water. Some method for supplementing the oxygen content of recreation lake water should, therefore, be provided for emergency use.

Conclusions

Turbidity, algae, and phosphate reduction of conventional oxidation pond water can be economically achieved. A practical tertiary process has been developed to supply boating and fishing lakes near Lancaster, Calif. The process selected and piloted at 30 g.p.m. features treatment with 200 to 300 mg./l. of alum, sedimentation, filtration, and chlorination. Phosphate is consistently reduced from 40 mg./l. to less than 0.5 mg./l. and algae counts from several hundred thousand to a few thousand per milliliter. Product water has been evaluated in the laboratory and in large simulated lakes stocked with fish. Algae slowly grow to high concentrations in the water but the rate of biological activity does not deplete the oxygen supply, or interfere with fish life, or cause nuisances. Laboratory stimulated growth tests show that algae growth rates are inhibited at phosphate concentrations less than 0.5 mg./l. and almost stop at less than 0.05 mg./l. The ecology of the simulated lake is typical of a fresh water environment supplied with limited nutrients.

ADDITIONAL READING

Cohen, J. M., "Improved Jar Test Procedure," *J. Am. Water Works Assoc.* **49** (11), pp. 1425–31 (1957).

Malhotra, S. K., et al., "Nutrient Removal from Secondary Effluents by Alum Flocculation and Lime Precipitation," *Intern. J. Air-Water Pollution* **8,** 487–500 (1964).

Merrell, J. C., Jr., and Katko, A., "Reclaimed Waste Water for Santee Recreational Lake," *Calif. Water Pollution Control Assoc. Bull.* **2** (3), 10–15 (Jan. 7, 1966).

Sawyer, C. N., "Fertilization of Lakes by Agricultural and Urban Drainage," *J. New Engl. Water Works Assoc.* **61,** 109–127 (1947).

CURRENT RESEARCH

Model for Predicting Pressure Drop and Filtration Efficiency in Fibrous Media

Lloyd Spielman and Simon L. Goren

Department of Chemical Engineering, University of California, Berkeley, Calif. 94720

■ Brinkman's model for flow through unconsolidated porous media is applied to flow through fibrous media to predict pressure drop for several different internal arrangements of the fibers. The essence of the model is that, on the average, the fluid in proximity to an obstacle embedded in a porous medium experiences, in addition to the usual force terms, a body damping force proportional to the local velocity accounting for the influence of neighboring objects on the flow. Implications of the model for correlating pressure drop and filtration efficiency are given.

The importance of fibrous filters in the removal of particulate matter from fluids is well known and has served as the motivation for numerous studies on the pressure drop and filtration efficiency for flow through fibrous media. The theory of aerosol filtration by fibrous filters has been comprehensively reviewed recently by Pich (1966) and Dorman (1966). Some articles published since these reviews include Stechkina and Fuchs (1966), Friedlander (1967), Kirsch and Fuchs (1967), May and Clifford (1967), Yoshioka, Emi, *et al.* (1967a), and Yoshioka, Emi, *et al.* (1967b). The theory of water filtration has been reviewed recently by Sakthivadivel and Irmay (1966) and O'Melia and Stumm (1967).

As a result of numerous experimental studies, notably that of Chen (1955) for continuum flow and that of Stern, Zeller, *et al.* (1960) for slip flow, it is now well established that for low speed Newtonian flow through fibrous filters, the pressure drop follows Darcy's law in being proportional to the fluid viscosity, the superficial velocity, and the filter thickness:

$$\Delta p = -k\mu U \Delta L \tag{1}$$

The coefficient of proportionality depends only on the medium geometry for continuum flow, and also on the gas mean free path for slip flow, but is independent of the fluid density.

Langmuir (1942) used the theoretical results of Lamb (1932) for low speed flow past an isolated cylinder to describe flow near a fiber within a filter. Since the Stokes' equations of creeping flow do not permit a solution for flow past an isolated cylinder, Lamb's solution necessarily incorporates inertial effects. Use of the Lamb solution to predict the pressure drop through a fibrous filter, therefore, leads to an expression which contains the fluid density and conflicts with the experimental validity of Darcy's law. Langmuir, therefore, sought a different method to describe the pressure drop but retained Lamb's velocity profile to predict particle capture within the medium.

Since k is independent of the Reynolds number, at least for sufficiently small Reynolds numbers, it may be concluded that Stokes' equations of creeping flow govern the motion of the fluid in the medium, and that the fiber boundaries in the vicinity of any given fiber must affect the fluid motion around that fiber in such a way that inertial effects remain negligible when compared with viscous effects throughout the entire region of flow. Further, Langmuir's expression for particle capture as well as expressions given in many subsequent treatments contain an unrealistic dependence on the Reynolds number. Accordingly, several models based on the equations of creeping flow have been proposed to justify Darcy's law for fibrous mats to give the dependence of the coefficient on the geometry of the medium and to give consistent expressions for particle capture. These include the cell models of Happel (1959) and Kuwabara (1959) as employed by Fuchs and Stechkina (1963) and Stechkina and Fuchs (1966). There are also treatments of flow longitudinal to regular arrays of circular cylinders by Emersleben (1925) and Sparrow and Loeffler (1959), which consider flow in a restricted region. These have been reviewed by Happel and Brenner (1965).

The present paper gives calculations of the pressure drop and filtration efficiency for flow in fibrous media based on the solution of another model. The model is that initially employed by Brinkman (1947a) to describe flow through a swarm of spheres and which was used successfully to calculate hindered settling velocities. The model was also used by Debye and Bueche (1948) to predict certain hydrodynamic

properties of dissolved polymer molecules. The essence of the model is that, on the average, the fluid in proximity to an obstacle embedded in a porous medium experiences a body damping force proportional to the velocity in addition to viscous and pressure forces, the damping force accounting for the influence of neighboring objects on the flow. The equation of motion is taken to be

$$\nabla p = \mu \nabla^2 \vec{u} - \mu \underline{k} \cdot \vec{u} \qquad (2)$$

where $\vec{u}$ is the average velocity field, p is the average pressure field, and $\underline{k}$ is a tensor giving the damping coefficients. The term average as used above refers to an ensemble average over all possible arrangements of the surrounding elements about a fixed central element permitted by the geometry of the medium. The damping coefficient, $\underline{k}$, is taken to be the Darcy resistance coefficient of the medium (inverse of the permeability) so that far from the obstacle where gradients of velocity vanish on the average, Equation 2 reduces to the differential form of Darcy's equation. The coefficient $\underline{k}$ is not determined empirically but is deduced theoretically for several representative mat geometries by relating the appropriate Darcy coefficient for a given geometry to the total drag on the individual elements comprising the porous medium. In the present case, the elements are fibers as represented by circular cylinders.

The essential difference between the cell models and the Brinkman hypothesis is that the cell models account for neighboring fiber influence by means of a microscopic envelope around the central fiber, the characteristic envelope size depending on the macroscopic voids, whereas the Brinkman hypothesis implies that the neighboring fibers damp the ensemble average microscopic flow near the central fiber in precisely the same way that the fibers of the medium damp local flow through the medium when averaged over all conceivable fiber arrangements.

From this latter consideration, the validity of Brinkman's hypothesis may be expected to be limited to conditions where the neighboring fibers are distributed about the central fiber in approximately the same way as they are generally distributed in the medium. The hypothesis therefore breaks down when applied to media of sufficiently low porosity because the effect of many solid boundaries in the immediate proximity to the central object cannot be well described by a simple damping term with spatially and directionally constant damping coefficients. For the case of packed spheres, Brinkman (1947b) has shown that allowing a simple spatial variation of the damping coefficient enables extension of the model to low porosities but at the expense of introducing a semiempirical fitting parameter.

The model also breaks down when applied to media having sufficiently high porosity at a given superficial velocity, or conversely, at a sufficiently high velocity for a given porosity. Then inertial effects become important and Darcy's law no longer describes the flow. For extremely porous media, the fibers behave effectively as isolated cylinders and Lamb's solution should then apply (Chen, 1955). The preponderance of literature dealing with fibrous media shows that the occurrence of fibrous media with voids fraction much below 0.8 is rare and, in fact, most filter mats and papers contain voids between 0.9 and about 0.99. For this reason, the theory presented here should be of almost completely general utility in practical applications since it is believed to apply in the range of voids mentioned.

Rigorous theoretical justification of Brinkman's equation has not yet been accomplished. An appeal to stochastic arguments would appear necessary since the microscopic flow field predicted by the model is intended to apply to an ensemble average of all permitted arrangements of fibers surrounding a fixed central fiber and not to any one particular arrangement. In a recent review by Brenner (1966), the theoretical basis of equations similar to Equation 2 is discussed in some detail but the justification for application to predicting flow fields at the microscopic scale of the medium is still lacking. Let it suffice here to say that very near the central fiber where the fluid velocity is small, the damping forces will be negligible when compared with the viscous forces and Equation 2 reduces to the Stokes' equation of creeping flow. Far from the fiber, where velocity gradients vanish (on the average), Equation 2 reduces to Darcy's equation. Brinkman's equation is seen to be the simplest postulate enabling these two limiting forms. Its validity in the region where both terms are of similar magnitude is open to question.

The model possesses the distinct advantage, over alternate models, of immediate applicability to filters composed of fibers with nonuniform fiber diameters and to filters where the fibers have distributed orientations with respect to the direction of flow. It may also be applied to mixtures of geometrical particles, such as fibers and spheres, and thereby provide a treatment of nonstationary filtration. The extension to nonuniform fiber diameters will be dealt with in a subsequent communication.

Here, calculations will be given for four orientation distributions that would be expected from the techniques ordinarily employed in preparing fiber mats. These orientations are:

Fiber axes all lying in planes perpendicular to the direction of the superficial velocity, but having completely random angles in those planes.

Fiber axes all parallel to the direction of the superficial velocity.

Fiber axes all lying in planes parallel to the direction of the superficial velocity, but having completely random angles in those planes.

Fiber axes completely randomly oriented in all directions.

The first case is of great practical importance since many fibrous media are prepared by depositing fibers onto a flat surface with their axes almost completely parallel to the surface. A good example is filter paper prepared by passing a slurry of fibers through a screen on which the fibers are deposited. Mats made by such a technique usually result in fiber axes lying at random angles within the parallel planes in which they fall. The third case is encountered with media prepared as above, but where flow is now in the direction parallel to the planes in which the fibers fall. The fourth case would approximate media prepared by essentially random packing of bulk fiber. The second case is of interest because it provides a limiting extreme for fibrous media and also because some experimental data are available for comparison (Sullivan, 1942).

The question may here arise as to whether or not the theoretical model can discern two arrays of fibers each of which has all fiber axes perpendicular to the direction of flow, the first having fibers at random angles to one another in planes perpendicular to the flow, while the second has its fiber axes parallel to one another in planes perpendicular to the direction of flow. Take the axis of a particular cylinder as the z-axis

in Cartesian coordinates and x normal to the planes in which the fibers lie. Apparently for the former situation, the average properties of the medium in the x- and y-directions are somewhat different from one another—that is, a velocity vector in the x-direction sees only fiber axes perpendicular to its own direction, whereas a vector in the y-direction sees fibers randomly oblique to its own direction. It can therefore be argued that a directional dependence of the damping coefficient $\underline{k}$ in Equation 2 should be considered in the analysis for this situation. In the second situation, no such difference in the x- and y-direction exists and, statistically, radial symmetry of the medium about the z-axis is expected in this case. In the subsequent analysis, the coefficient $\underline{k}$ will be assumed constant with direction and, strictly speaking, the analysis would be expected to apply rigorously only to the case where the axes of the fibers are all parallel to one another. However, the predicted flow profile is not very sensitive to the absolute value of the coefficient $\underline{k}$ and for the former case where variation of $\underline{k}$ in the x- and y-directions is expected, this variation is of such a magnitude that it would not be expected to affect the flow profile around a single fiber to any significant extent. This is not to imply that orientation effects are being ignored, but that the significant effect is obtained by considering the distribution of angles of the individual fibers themselves and not so much the directional properties of the medium surrounding an average fiber. The preceding argument may be summarized by stating that in the subsequent analysis no distinction between the two discussed situations of flow perpendicular to fiber axes will be made and that both can be described by a single damping coefficient. If an analysis allowing a directional dependence of $\underline{k}$ were carried out the numerical result is expected to be very close to that obtained by ignoring the directional variation of $\underline{k}$ as a first approximation. Such an analysis is not carried out here owing to the mathematical complexity.

Because of the availability of very small fibers ($d_f \sim 0.1\mu$) and their use to produce extremely effective filters, calculations are given for the slip flow regime—i.e., when the Knudsen number is small but not negligible.

The velocity fields thus computed are used to predict pressure drop for flow through fibrous mats. In addition, when the interception number is small and the Peclet number is large, certain results of previous theoretical studies are directly applicable in the absence of slip for particle deposition by interception and Brownian diffusion.

Calculation of the Velocity Profiles. The average motion for incompressible flow around an individual fiber embedded in a fibrous medium is described by Brinkman's equation, extended to include the directional properties of the medium:

$$\nabla p = \mu \nabla^2 \vec{u} - \mu \underline{k} \cdot \vec{u} \tag{2}$$

together with the equation of continuity

$$\nabla \cdot \vec{u} = 0 \tag{3}$$

The boundary conditions are that far from the surface of the cylinder the average velocity is a constant:

$$\vec{u} = \vec{U} \text{ at } r = \infty \tag{4}$$

while at the surface of the cylinder, $r = a$,

$$\vec{u} \cdot \vec{n} = 0 \tag{5}$$

and

$$\vec{u} \cdot \vec{t} = \frac{\text{Kn}'}{1 + \text{Kn}'} \vec{n} \cdot \nabla(\vec{u} \cdot \vec{t}) \tag{6}$$

$\text{Kn}' = c_m \text{Kn} = c_m \lambda / a$ is a modified Knudsen number, where c_m is a parameter usually of the order of unity that characterizes the interaction of the gas molecules with the solid surface.

The flow past a given cylinder may be resolved into two parts, $\vec{u}_1$ and $\vec{u}_2$, where $\vec{u}_1$ is the velocity field normal to the axis of the cylinder and $\vec{u}_2$ is parallel to the axis of the cylinder. For any of the geometrical arrangements discussed above, because of the symmetry properties of the media and the additional assumptions made, the problem for the two flow fields can be solved separately—i.e.,

$$\nabla p_1 = \mu \nabla^2 \vec{u}_1 - \mu k_1 \vec{u}_1 \tag{7}$$

$$\nabla p_2 = \mu \nabla^2 \vec{u}_2 - \mu k_2 u_2 \tag{8}$$

where k_1 and k_2 are scalar constants whose values depend upon the geometry of the mat. Numerical values for these constants will be determined after the drag per unit length of fiber has been expressed in terms of them. The continuity equation and boundary conditions also hold for each field separately.

In case 1, $(p_1, \vec{u}_1) \neq 0$, $(p_2, \vec{u}_2) = 0$, $k_1 \neq k_2$

In case 2, $(p_1, \vec{u}_1) = 0$, $(p_2, \vec{u}_2) \neq 0$, $k_1 \neq k_2$

In case 3, $(p_1, \vec{u}_1) \neq 0$, $(p_2, \vec{u}_1) \neq 0$, $k_1 = k_2$

In case 4, $(p_1, \vec{u}_1) \neq 0$, $(p_2, \vec{u}_2) \neq 0$, $k_1 = k_2$

The solution for the field $(p_1, \vec{u}_1)$ is readily found by assuming the pressure and stream function in cylindrical coordinates are of the form

$$p_1 = g(r) \cos \theta \tag{9}$$

and

$$\Psi = U_1 f(r) \sin \theta \tag{10}$$

so that

$$u_{1r} = \frac{1}{r} \frac{\partial \Psi}{\partial \theta} = U_1 \frac{f}{r} \cos \theta \tag{11}$$

$$u_{1\theta} = -\frac{\partial \Psi}{\partial r} = -U_1 \frac{df}{dr} \sin \theta \tag{12}$$

where U_1 is the velocity component normal to the cylinder at a great distance from its surface. In what follows, the subscript on k_1 will be suppressed. In view of the continuity equation, the divergence of Equation 7 shows that the pressure obeys Laplace's equation

$$\frac{\partial^2 p_1}{\partial r^2} + \frac{1}{r} \frac{\partial p_1}{\partial r} + \frac{1}{r^2} \frac{\partial^2 p_1}{\partial \theta^2} = 0 \tag{13}$$

so that

$$p_1 = \{Ar^{-1} + Br\} \cos \theta + \text{constant} \tag{14}$$

where A and B are constants of integration. Substitution of Equations 11, 12, and 14 into the r component of Equation 7 gives the following equation for $f(r)$:

$$\frac{d^2}{dr^2}\left(\frac{f}{r}\right) + \frac{3}{r} \frac{d}{dr}\left(\frac{f}{r}\right) - k\frac{f}{r} = \frac{A}{\mu U_1 r^2} - \frac{B}{\mu U_1} \tag{15}$$

The general solution to this equation is

$$f(r) = -\frac{A}{\mu U_1 kr} + \frac{Br}{\mu U_1 k} - CK_1(k^{1/2}r) - DI_1(k^{1/2}r) \quad (16)$$

where C and D are constants of integration and $I_p(x)$ and $K_p(x)$ are the modified Bessel functions of order p and argument x. The conditions

$$u_{1r} \to U_1 \cos\theta, \; u_{1\theta} \to U_1 \sin\theta \text{ as } r \to \infty \quad (17)$$

require

$$D = 0 \quad (18)$$

and

$$B/\mu U_1 k = 1 \quad (19)$$

The boundary conditions at the surface of the cylinder require

$$C/a = -2G(\text{Kn}', ka^2)/k^{1/2}aK_0(k^{1/2}a) \quad (20)$$

$$A/\mu U_1 ka^2 = 1 + 2G(\text{Kn}', ka^2) \times$$
$$K_1(k^{1/2}a)/k^{1/2}aK_0(k^{1/2}a) \quad (21)$$

where

$$G(\text{Kn}', ka^2) = \frac{1 + 2\text{Kn}'}{1 + \text{Kn}'[2 + k^{1/2}aK_1(k^{1/2}a)/K_0(k^{1/2}a)]} \quad (22)$$

The drag per unit length of fiber is found by integrating the total stress acting on the cylinder surface:

$$F_D = \int_0^{2\pi} \left\{ p_1(a)\cos\theta - \tau_{r\theta}(a)\sin\theta \right\} a d\theta \quad (23)$$

where

$$\tau_{r\theta} = -\mu \left\{ r\frac{\partial}{\partial r}(u_\theta/r) + \frac{1}{r}\frac{\partial}{\partial\theta} u_r \right\} \quad (24)$$

Carrying out the indicated operations gives

$$F_{D_1}/4\pi\mu U_1 = \frac{1}{2} ka^2 + G(\text{Kn}', ka^2)\left\{1 + k^{1/2}aK_1(k^{1/2}a)/\right.$$
$$\left. K_0(k^{1/2}a)\right\} - 1 \equiv \Phi_1(\text{Kn}', ka^2) \quad (25)$$

When slip effects are completely negligible $\text{Kn}' = 0$, and this reduces to

$$F_{D_1}/4\pi\mu U_1 = \frac{1}{2} ka^2 + k^{1/2}aK_1(k^{1/2}a)/K_0(k^{1/2}a) \equiv$$
$$\Phi_1(0, ka^2) \quad (26)$$

The solution for the field $(p_2, \vec{u}_2)$ for flow parallel to a fiber is readily found since there is only one component of velocity, u_{2_z}. It is, again suppressing the subscript on k_2,

$$u_{2_z} = U_2 \left[1 - \frac{K_0(k^{1/2}r)}{K_0(k^{1/2}a) + \text{Kn}'(1 + \text{Kn}')^{-1}k^{1/2}aK_1(k^{1/2}a)} \right] \quad (27)$$

where U_2 is the velocity parallel to the cylinder at a large distance from its surface. The drag force per unit length of fiber is given by

$$F_{D_2}/4\pi\mu U_2 = \frac{1}{2} [K_0(k^{1/2}a)/k^{1/2}aK_1(k^{1/2}a) +$$
$$\text{Kn}'/(1 + \text{Kn}')]^{-1} \equiv \Phi_2(\text{Kn}', ka^2) \quad (28)$$

When slip effects are completely negligible $\text{Kn}' = 0$, and this result reduces to

$$F_{D_2}/4\pi\mu U_2 = \frac{1}{2} k^{1/2}aK_1(k^{1/2}a)/K_0(k^{1/2}a) \equiv \Phi_2(0, ka^2) \quad (29)$$

Calculation of the Darcy Resistance Coefficient for the Various Mat Geometries. If Ψ is the angle between a cylinder axis and the direction of the superficial velocity, then the drag component in the direction of flow per unit length of fiber is

$$F_D = F_{D_1}\sin\Psi + F_{D_2}\cos\Psi \quad (30)$$

For case 1, where all fibers have their axes perpendicular to the superficial velocity—i.e., $\Psi = \pi/2$ for all fibers—the pressure drop in the direction of flow is obtained by multiplying the drag force per unit fiber length by the total length of fiber per unit volume of mat, $\alpha/\pi a^2$, giving

$$-\frac{dP}{dL} = F_{D_1}\cdot\alpha/\pi a^2 = \mu kU \quad (31)$$

The last equality follows from Darcy's law. Substitution of F_{D_1} from Equation 25 gives

$$ka^2 = 4\alpha\Phi_1(\text{Kn}', ka^2) \quad (32)$$

which is the desired relationship between the Darcy coefficient and the filter geometry for case 1.

For case 2, where fibers are all parallel to the superficial velocity—i.e., $\Psi = 0$ for all fibers—a similar calculation gives

$$ka^2 = 4\alpha\Phi_2(\text{Kn}', ka^2) \quad (33)$$

For fibers oblique to the direction of flow in cases 3 and 4, since $k_1 = k_2$ there is no need to append a subscript on the Darcy coefficient. The substitution of F_{D_1} and F_{D_2} from Equations 25 and 28 into Equation 30 gives

$$F_D = 4\pi\mu[\Phi_1(\text{Kn}', ka^2)U_1\sin\Psi +$$
$$\Phi_2(\text{Kn}', ka^2)U_2\cos\Psi] \quad (34)$$

Elimination of U_1 and U_2 by means of the expressions

$$U_1 = U\sin\Psi \qquad U_2 = U\cos\Psi \quad (35)$$

gives

$$F_D = 4\pi\mu U(\Phi_1\sin^2\Psi + \Phi_2\cos^2\Psi) \quad (36)$$

For case 3, the normalized frequency function giving the length fraction of fibers having orientations between Ψ and $\Psi + d\Psi$ is

$$p(\Psi)d\Psi = \frac{2}{\pi} d\Psi \quad (37)$$

Ψ varies from 0 to $\pi/2$. The pressure drop in the direction of flow is obtained by averaging Equation 36 with this weighting function and then multiplying by the total fiber length per unit volume, giving

$$-\frac{dP}{dL} = \frac{\alpha}{\pi a^2} \cdot 4\pi\mu U \left(\frac{1}{2}\ \Phi_1 + \frac{1}{2}\ \Phi_2\right) \tag{38}$$

The Darcy coefficient is therefore given by

$$ka^2 = 4\alpha\left[\frac{1}{2}\ \Phi_1(\mathrm{Kn}', ka^2) + \frac{1}{2}\ \Phi_2(\mathrm{Kn}', ka^2)\right] \tag{39}$$

For case 4, where the fibers are isotropically random in their orientations,

$$p(\Psi)d\Psi = \sin\Psi d\Psi \tag{40}$$

giving

$$ka^2 = 4\alpha\left[\frac{2}{3}\ \Phi_1(\mathrm{Kn}', ka^2) + \frac{1}{3}\ \Phi_2(\mathrm{Kn}', ka^2)\right] \tag{41}$$

Each of the above four cases may be represented by

$$ka^2 = 4\alpha\Phi(\mathrm{Kn}', ka^2) \tag{42}$$

where Φ is the appropriate linear combination of Φ_1 and Φ_2. The function Φ of Equation 42 is transcendental but still of closed form. Use of Equation 42 appears to be inconvenient at first sight since ka^2 is determined implicitly as a function of α and Kn'. However, since Equation 42 is explicit in α, curves of ka^2 vs. α (at fixed Kn') are easily generated, and the implicit occurrence of ka^2 presents no real difficulty. By contrast, other models usually yield expressions which are explicit in ka^2 and implicit in α.

Since the no-slip forms of Equations 32, 33, 39, and 41 are particularly concise and of considerable importance, they are given separately below.

For case 1, $ka^2 = 4\alpha\left[\frac{1}{2}\ ka^2 + k^{1/2}aK_1(k^{1/2}a)/K_0(k^{1/2}a)\right]$

$$\tag{32'}$$

For case 2, $ka^2 = 4\alpha\left[\frac{1}{2}\ k^{1/2}aK_1(k^{1/2}a)/K_0(k^{1/2}a)\right] \tag{33'}$

For case, 3, $ka^2 = 4\alpha\left[\frac{1}{4}\ ka^2 + \frac{3}{4}\ k^{1/2}aK_1(k^{1/2}a)/K_0(k^{1/2}a)\right]$

$$\tag{39'}$$

For case 4, $ka^2 = 4\alpha\left[\frac{1}{3}\ ka^2 + \frac{5}{6}\ k^{1/2}aK_1(k^{1/2}a)/K_0(k^{1/2}a)\right]$

$$\tag{41'}$$

Criterion for Creeping Flow in Fibrous Media. Analysis of Equation 2 and its solutions for large r provides an interesting and useful criterion for the applicability of Darcy's law to fibrous media. Equation 2 assumes that fluid inertia is negligible throughout the entire region of flow about the central fiber. Near the cylinder this assumption is valid if $\mathrm{Re} \ll 1$ because of the dominance of viscous forces over inertia even though the damping force is usually negligible here. The asymptotic forms of Equations 16 through 22 for large r indicate that the mean viscous forces are of order $\mu U/r^2$, the mean inertial forces are of order $\rho U^2/r$, and the damping force is of order μkU. Thus, at sufficiently large r the damping force dominates the inertial forces, and these in turn dominate the viscous forces. The question is whether the damping forces still dominate the inertial forces in the region where the inertial and viscous forces are of comparable magnitude—i.e., for $r \approx \mu/\rho U$. For this value of r, the ratio of the inertial forces to the damping force is Re^2/ka^2. Thus, the condition that inertial forces be negligible in the intermediate region is $\mathrm{Re}^2/ka^2 \ll 1$. This condition shows that even for very small fiber Reynolds numbers inertial effects can become important if the medium is sufficiently porous.

Results for Pressure Drop. Typical results of the present theory are shown in Figures 1, 2, and 3 where the dimensionless pressure drop

$$\Phi(\mathrm{Kn}', ka^2) = ka^2/4\alpha = \Delta pa^2/4\alpha\mu U\Delta L$$

is plotted as a function of the fraction solids α. Several authors have correlated their experimental data in terms of the group, $\frac{1}{2}C_{D\alpha}N_{\mathrm{Re}}$, which is equal to $4\pi(1 - \alpha)\Phi$ and which is shown on the right-hand side of the figures. Figure 1 shows the results for no slip for the four mat geometries considered here. Figure 2 compares the predictions for the most important geometry—namely, all fibers normal to the flow with no slip—with those of Kuwabara (1959) and Happel (1959) and an empirical equation of Davies (1952). Davies' equation correlates the pressure drop measurements for low Reynolds number flow through a variety of fibrous materials with fraction solids in the range 0.006 to 0.3. The present model predicts lower pressure drops than the Happel and Kuwabara models for $\alpha < 0.1$ and is in better agreement with the empirical equation. In fact, the present theory and Davies' equation are practically coincident for $0.02 < \alpha < 0.06$. The present model gives higher pressure drops for $\alpha > 0.13$ than does the Happel model and for $\alpha > 0.21$ than does the Kuwabara model. In recent experiments, Kirsch and Fuchs (1967) found that pressure drop for flow through regular arrays of fibers was best correlated by Kuwabara's results; however, introducing irregularities into the array at the same fraction solids resulted in a lower pressure drop. In general, other data from the literature fall lower than all the theoretical predictions, and since the model presented here yields the lowest values in its range of validity, it is believed to be a better theory for flow through random fibrous media than the cell models. Further evidence for this will be provided in the communication dealing with mixtures of fiber diameters.

Figure 3 shows the effect of slip on reducing the pressure drop when the fiber axes are all normal to the flow. For example, for $\mathrm{Kn}' = 0.2$ the pressure drop is reduced to approximately 0.7 of the no-slip value; this factor is relatively independent of α. Although the theory is strictly limited to small Knudsen numbers, the authors have also shown its predictions for $\mathrm{Kn}' = 1$ and ∞ to get a rough idea of the reduction for these values.

Aerosol Filtration by Interception and Brownian Diffusion. Beginning with the work of Langmuir (1942), numerous authors have attempted to predict particle removal by fibrous media by considering the interaction of different mechanisms for deposition with the flow field near a single fiber. Therefore,
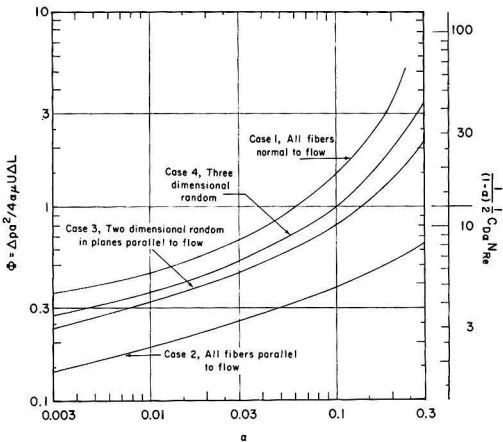
Figure 1. Theoretical predictions of dimensionless pressure gradient *vs.* volume fraction fibers for different fiber orientations
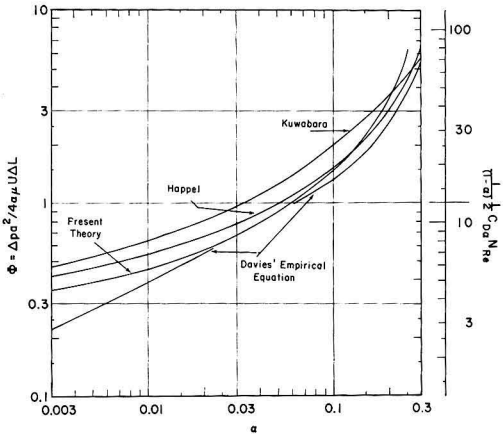

Figure 2. Dimensionless pressure gradient *vs.* volume fraction fibers for fiber axes all perpendicular to direction of flow, comparing cell models and present theory with Davies' empirical relation
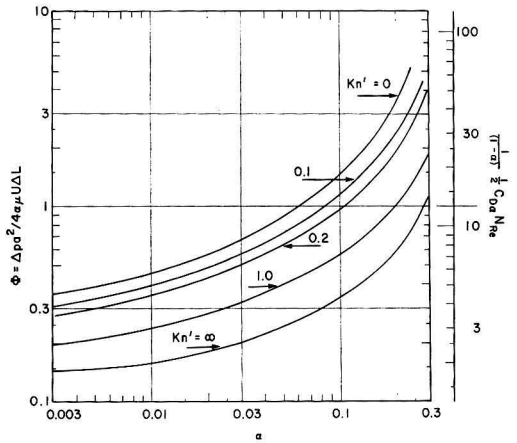

Figure 3. Theoretical predictions of dimensionless pressure gradient *vs.* volume fraction fibers for different Knudsen numbers and where fiber axes are all perpendicular to the direction of flow

certain of the ingenious analyses of these previous workers are applied to predict particle removal by interception and Brownian diffusion interacting with the flow field predicted in accordance with Brinkman's model with no slip. Of course, other effects such as inertial impaction or electrostatic attraction can play significant roles under certain practical conditions, but these mechanisms will not be discussed here.

Consider first the geometry where all fiber axes are normal to the flow. Most computations are based upon velocity fields having one of the two forms

$$\Psi = \frac{Ua}{2\zeta} \left\{ \frac{r}{a} - \frac{a}{r} - 2\frac{r}{a} \ln \frac{r}{a} \right\} \sin \theta \qquad (43)$$

or

$$\Psi = \frac{Ua}{\xi} \left\{ \frac{r}{a} - 1 \right\}^2 \sin \theta \qquad (44)$$

where ζ and ξ are coefficients depending on the particular flow model used.

Equation 43 describes the stream function given by Lamb when $\zeta = [2 - \ln (2aU/\nu)]$. In the limit of very high porosity, the cell models of Happel and Kuwabara have the same form provided $\zeta = \left[-\frac{1}{2} \ln \alpha - 0.5 \right]$ and $\zeta = \left[-\frac{1}{2} \ln \alpha - 0.75 \right]$, respectively. The stream function given by Equation 16 with no slip can also be reduced to this same form by expanding the Bessel functions for small values of their arguments. The coefficient is then

$$\zeta = K_0(k^{1/2}a) \cong - \ln \left(\frac{1}{2} k^{1/2}a \right) - 0.5772 \qquad (45)$$

The expansion of the Bessel functions for small arguments restricts the analysis, employing Equation 43, to very high porosities. This restriction is, however, no more severe than that required for representation of the Happel and Kuwabara cell models by Equation 43.

For low interception numbers and high Peclet numbers, it is possible to extend the analysis to more typical porosities since, in view of the thinness of the diffusion boundary layer, it is adequate to approximate the velocity field by using only the first term in a power series expansion about the fiber surface. With no slip, all models give approximate stream functions having the form of Equation 44. For Lamb's solution $\xi = [2 - \ln (2aU/\nu)]$; for Happel's model $\xi = \left[-\frac{1}{2} \ln \alpha - 0.5 + \alpha^2/2(1 + \alpha^2) \right]$; for Kuwabara's model $\xi = \left[-\frac{1}{2} \ln \alpha - 0.75 + \alpha - \alpha^2/4 \right]$; and the present theory gives

$$\xi = K_0(k^{1/2}a)/k^{1/2}aK_1(k^{1/2}a) \tag{46}$$

To the approximation implied by Equation 44, Friedlander (1967) and Stechkina and Fuchs (1966) showed by inspection of the convective diffusion equation that the efficiency η of a single fiber (defined as the actual collection rate per unit length of fiber divided by $2aUn$) due to simultaneous interception and Brownian diffusion is governed by a function of one variable:

$$\eta R Pe = F(R^3 Pe/\xi) \tag{47}$$

For very large values of the argument this goes over to the known result for interception only,

$$\eta = R^2/\xi \tag{48}$$

and for very small values of the argument, this becomes the expression for Brownian diffusion of "point" particles as discussed by Friedlander (1957) and Natanson (1957),

$$\eta = 2.9\xi^{-1/3}Pe^{-2/3} \tag{49}$$

using Natanson's value of the coefficient. Thus the two asymptotes of Equation 47 are known.

Stechkina and Fuchs (1966) treated combined interception and Brownian diffusion by numerically solving the convective diffusion boundary layer equation. They found they could fit their numerical results for the efficiency of a single fiber reasonably well with the following simple expression

$$2\zeta\eta = 2\zeta\eta_R + 2\zeta\eta_D + 2.48\zeta^{1/2}Pe^{-1/2}R^{2/3} \tag{50}$$

η_R and η_D are the efficiencies obtained for interception and diffusion acting separately as given by Fuchs and Stechkina (1963) and Stechkina (1965)

$$2\zeta\eta_R = 2(1 + R) \ln (1 + R) -$$
$$(1 + R) + (1 + R)^{-1} \tag{51}$$

$$2\zeta\eta_D = 5.8\zeta^{2/3}Pe^{-2/3} + 1.25\zeta Pe^{-1} \tag{52}$$

All of these results are based on a stream function having the form given by Equation 43. The form of the interaction term in Equation 50 is not consistent with the one-place function of Equation 47, expected in the limit of low interception number and large Peclet number. This is probably a result of the authors' attempt to fit their numerical results over the entire range of investigated interception numbers and Peclet numbers with only one interaction term.

The previous work on filter efficiency of a single fiber is immediately applicable to the flow field computed from Brinkman's equation when the fiber axes are normal to the direc-

tion of flow provided ζ and ξ are given by Equations 45 and 46 for very high and typical porosities, respectively. For the other mat geometries it is more appropriate to speak of a local rate of removal of particles per unit volume of filter Γ rather than a single fiber efficiency. Because of the long length of the fibers compared with their diameters, it may be assumed that component of flow along a fiber axis has only a minor influence on the particle capture rate since ends may be neglected for their contribution to particle capture, and axial gradients in particle concentration may be neglected as far as diffusion is concerned. Thus, only the component of flow normal to the fiber axes is of importance in determining the removal of particles, and for fibers whose axes are at an angle Ψ from the direction of flow Γ is given by

$$\Gamma = (\alpha/\pi a^2)(2aU \sin \Psi\, n\eta) \tag{53}$$

where η is given by the appropriate expression above, but with U replaced by $U \sin \Psi$ whenever it appears. To find the local rate of removal of particles per unit volume of filter for a given mat geometry, one must average this equation over all permitted values of Ψ using the appropriate distribution function. For interception only, at low interception numbers, Equation 48 leads to

$$\Gamma = \gamma_1(2\alpha Un/\pi a)(R^2\xi^{-1}) \tag{48'}$$

For Brownian diffusion only, at high Peclet numbers, Equation 49 leads to

$$\Gamma = \gamma_2(2\alpha Un/\pi a)(2.9\, Pe^{-2/3}\xi^{-1/3}) \tag{49'}$$

Stechkina and Fuchs' fitted expression for simultaneous interception and Brownian diffusion, Equation 50, becomes

$$\Gamma = \Gamma_R + \Gamma_D + \gamma_3(2\alpha Un/\pi a)(1.25\zeta^{-1/2}Pe^{-1/2}R^{2/3}) \tag{50'}$$

where the expressions of Fuchs and Stechkina for interception and diffusion acting separately lead to

$$\Gamma_R = \gamma_1(2\alpha Un/\pi a)[2(1 + R) \ln (1 + R) -$$
$$(1 + R) + (1 + R)^{-1}]\zeta^{-1} \tag{51'}$$

Table I. Coefficients for Computing Rate of Filtration per Unit Volume for Various Mat Geometries

Mat geometry	$\overline{(\sin \Psi)}$ $\parallel$ Coefficient γ_1	$\overline{(\sin \Psi)^{1/3}}$ $\parallel$ γ_2	$\overline{(\sin \Psi)^{1/2}}$ $\parallel$ γ_3	γ_4	γ_5
Case 1, all fibers normal to flow	1	1	1	1	2
Case 2, all fibers parallel to flow	0	0	0	$1/2$	0
Case 3, fiber axes two-dimensional random in planes parallel to flow	$2/\pi$	0.824	0.764	$3/4$	1
Case 4, fiber axes three-dimensional random	$\pi/4$	0.911	0.874	$5/6$	$4/3$
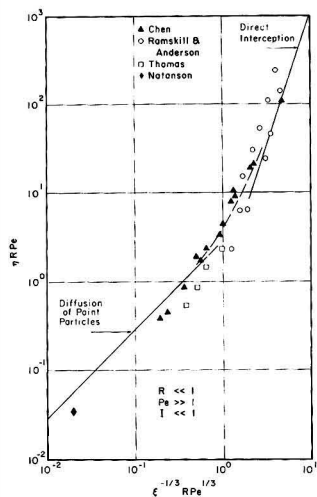
Figure 4. Comparison of selected data with theoretical predictions of particle collection by interception and diffusion, interpolated through the region of combined effects (dashed portion)

Impaction is assumed to be small as the impaction number $I = C_m \rho_p a_p^2 U / 9 \mu a$ is much less than unity
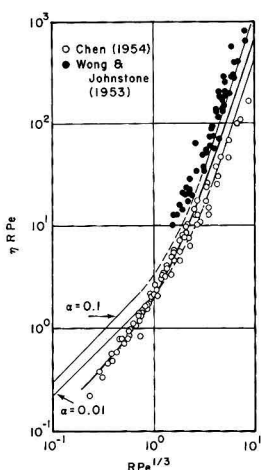

Figure 5. Comparison of Friedlander's correlation of selected data for collection by interception and diffusion with theoretical predictions at two different fiber volume fractions interpolated through the region of combined effects (dashed portion)

Data shown are for Re < 1, R < 1, I < 0.6

and

$$\Gamma_D = (2\alpha U n / \pi a)[\gamma_2(2.9 \text{ Pe}^{-2/3}\zeta^{-1/3}) + 0.62 \text{ Pe}^{-1}] \quad (52')$$

The values of the numerical coefficients γ_1, γ_2, and γ_3 for the four mat geometries considered are listed in Table I.

For the four mat geometries, the function ξ given by Equation 46 is easily related to the function Φ given in the plot of Figure 1 by means of Equations 32', 33', 39', and 41'. The relationships all take the form

$$\xi = \gamma_4 \cdot \frac{1}{(1 - \gamma_5 \alpha)\Phi} \quad (54)$$

where the coefficients γ_4 and γ_5 corresponding to the appropriate mat geometries are also given in Table I.

Comparison with Experiment. For the purpose of comparing theory with experiment, it was convenient to attempt to correlate literature data on filtration owing to interception and diffusion by means of Equation 47 and its exactly known asymptotes. This correlation is shown in Figure 4 and is very similar to that given by Friedlander (1967) except that the correlation presented here incorporates a theoretical porosity dependence. The plot includes selected data of Chen (1954), Ramskill and Anderson (1951), Thomas (1953), and Natanson and Ushakova (1961). The quality of the data in Figure 4 is not sufficiently high to enable decisive evaluation of the porosity dependence predicted here with that predicted by other theories, such as the cell models, since they should correlate the data equally well. The correlation does, however, substantiate the form given by Equation 47 with no adjustable parameters and the presence of an unrealistic Reynolds number dependence, as in Friedlander (1958), is eliminated.

Figure 5 shows the semiempirical correlation given by Friedlander, which contains no provision for porosity dependence. The porosity dependence for the data of Chen (1954) was empirically eliminated, whereas the data of Wong and Johnstone (1953) did not show significant variation over the range of solids fraction studied ($0.045 < \alpha < 0.098$). Figure 5 also shows the curves corresponding to $\alpha = 0.01$ and $\alpha = 0.1$, predicted by means of the theory presented here for the exactly known asymptotes and interpolated through the region of combined interception and diffusion.

Nomenclature

a	= cylinder (fiber) radius
a_p	= particle radius
c_m	= dimensionless slip flow parameter characterizing interaction of gas molecules with solid surface
D	= Brownian diffusivity
(r)	= function giving radial dependence of stream function
F_D	= drag force per unit length of cylinder
k	= Darcy resistance (damping) coefficient
k_1	= component of Darcy coefficient for flow normal to cylinder axis
k_2	= component of Darcy coefficient for flow parallel to cylinder axis
$\text{Kn, Kn}'$	$= \left(\dfrac{\lambda}{a}, \dfrac{c_m \lambda}{a}\right)$ = Knudsen numbers for fiber

L	=	distance into fibrous medium
n	=	particle concentration, No./vol.
p	=	pressure field
$p(\Psi)$	=	distribution of fiber angles of orientation
Pe	$= \dfrac{2aU}{D}$	= fiber Peclet number
r	=	radial coordinate measured from cylinder axis
R	$= \dfrac{a_p}{a}$	= interception parameter
Re	$= \dfrac{2aU\rho}{\mu}$	= fiber Reynolds number
$\bar{u}$	=	vector velocity field
$\bar{u}_1$	=	vector velocity field for flow normal to cylinder axis
$\bar{u}_2$	=	vector velocity field for flow parallel to cylinder axis
$\bar{U}$	=	velocity far from central cylinder
z	=	coordinate in direction parallel to cylinder axis
α	=	volume fraction of fiber in medium
$\gamma_1, \gamma_2, \gamma_3, \gamma_4, \gamma_5$	=	numerical constants given in Table I
Γ	=	rate of removal of particles per unit volume of medium
ζ	=	stream function parameter depending on flow model
θ	=	angular coordinate
λ	=	gas mean free path
μ	=	fluid viscosity
ξ	=	stream function parameter depending on flow model
ρ	=	fluid density
Φ (Kn$'$, ka^2), Φ_1, Φ_2	=	functions representing influence of slip flow and neighboring medium on drag acting upon central fiber (subscripts 1 and 2 refer to components of drag, respectively, normal and parallel to the axis)
$\tilde{\Psi}$	=	stream function for flow around cylinder
Ψ	=	angle between fiber axis and flow direction

Literature Cited

Brenner, H., *Advan. Chem. Eng.* **6**, 287 (1966).
Brinkman, H. C., *Appl. Sci. Res.* A1, 27 (1947a).
Brinkman, H. C., *Appl. Sci. Res.* A1, 81 (1947b).
Chen, C. Y., "Filtration of Aerosols by Fibrous Media," Annual Report, Contract DA 18-108-CML-4789, U. S. Army Chemical Corps, Eng. Expt. Station, University of Illinois, 1954.
Chen, C. Y., *Chem. Rev.* **55,** 595 (1955).
Davies, C. N., *Inst. Mech. Engrs. (London), Proc.* 1B, 185 (1952).
Debye, P., Bueche, A. M., *J. Chem. Phys.* **16**, 573 (1948).
Dorman, R. G., "Aerosol Science," C. N. Davies, Ed., Chap. VIII, Academic Press, New York, 1966.
Emersleben, O., *Physik. Z.* **26**, 601 (1925).
Friedlander, S. K., *A.I.Ch.E. J.* **3**, 43 (1957).
Friedlander, S. K., *Ind. Eng. Chem.* **50**, 1161 (1958).
Friedlander, S. K., *J. Colloid Interface Sci.* **23**, 157 (1967).
Fuchs, N. A., Stechkina, I. B., *Ann. Occup. Hyg.* **6**, 27 (1963).
Happel, J., *A.I.Ch.E. J.* **5**, 174 (1959).
Happel, J., Brenner, H., "Low Reynolds Number Hydrodynamics," Prentice-Hall, Englewood Cliffs, N. J., 1965.
Kirsch, A. A., Fuchs, N. A., *Ann. Occup. Hyg.* **10**, 23 (1967).
Kuwabara, S., *J. Phys. Soc. Japan* **14**, 527 (1959).
Lamb, H., "Hydrodynamics," 6th ed., Cambridge University Press, 1932.
Langmuir, I., *OSRD Rept.* No. **865**, 1942.
May, K. R., Clifford, R., *Ann. Occup. Hyg.* **10**, 83 (1967).
Natanson, G. L., *Dokl. Akad. Nauk SSSR* **112**, 100 (1957).
Natanson, G. L., Ushakova, E. N., *Russ. J. Phys. Chem.* **35**, 224 (1961).
O'Melia, C. R., Stumm, W., "Theory of Water Filtration," paper presented at Annual Conference of Am. Water Works Assoc., Atlantic City, N. J., 1967.
Pich, J., "Aerosol Science," C. N. Davies, Ed., Chap. IX, Academic Press, New York, 1966.
Ramskill, E. A., Anderson, W. L., *J. Colloid Sci.* **6**, 416 (1951).
Sakthivadivel, R., Irmay, S., "A Review of Filtration Theories," Rept. HEL 15-4 of Hydraulic Eng. Lab., University of California, Berkeley, Calif., 1966.
Sparrow, E. M., Loeffler, A. L., Jr., *A.I.Ch.E. J.* **5**, 325 (1959).
Stechkina, I. B., *Dokl. Akad. Nauk SSSR* **167**, 1327 (1965).
Stechkina, I. B., Fuchs, N. A., *Ann. Occup. Hyg.* **9**, 59 (1966).
Stern, S. C., Zeller, H. W., Schekman, A. I., *J. Colloid Sci.* **15**, 546 (1960).
Sullivan, R. R., *J. Appl. Phys.* **13**, 725 (1942).
Thomas, D. G., Ph.D. thesis in chemical engineering, Ohio State University, 1953.
Wong, J. B., Johnstone, H. F., "Collection of Aerosols by Fiber Mats," Tech. Rept. No. 11, Eng. Expt. Station, University of Illinois, 1953.
Yoshioka, N., Emi, H., Fukushima, M., *Kagaku Kogaku* **31**, 157 (1967a).
Yoshioka, N., Emi, H., Sone, H., *Kagaku Kogaku* **31**, 1011 (1967b).

Particle-Size Distribution of Metal Components in Urban Air

Robert E. Lee, Jr., Ronald K. Patterson, and Jack Wagman

U. S. Department of Health, Education, and Welfare, Public Health Service, Bureau of Disease Prevention and Environmental Control, Control Technology Research and Development Program, National Center for Air Pollution Control, Cincinnati, Ohio 45202

■ Concentration and particle-size distribution of six suspended metals (iron, lead, cadmium, chromium, magnesium, and copper) were measured in downtown Cincinnati and in Fairfax, a Cincinnati suburb. Particulate was collected and size-fractionated in cascade impactors; the metals were extracted with acids and analyzed by atomic absorption spectrophotometry. Samples obtained from the two locations exhibited different particle-size distributions; at both locations, however, only lead was predominantly submicron. Concentrations of the metals were typically three to five times higher in Cincinnati than in Fairfax; magnesium concentrations were about 17 times higher.

$\mathbf{M}$easurements of particle-size distribution of the chemical components of suspended particulate in ambient air are scarce despite the known importance of particle size in such effects as pulmonary penetration and retention (Dautrebande, 1962), visibility reduction in the atmosphere (Middleton, 1952), and particle-particle and particle-gas interactions. The steady increase in the number of automobiles, manufacturing facilities, and other sources that emit metals heightens the need for data on both concentrations and particle-size distributions of metal contaminants in the air. These data will provide a basis for assessing the degree of hazard posed by increasing emissions.

In the work reported here, the concentrations and particle-size distributions of iron, lead, cadmium, magnesium, copper, and chromium were measured by atomic absorption spectrophotometric analysis of 24-hour samples obtained in downtown Cincinnati. Size distributions were also measured in longer-term samples collected in Fairfax, a suburb of Cincinnati.

Experimental

The Cincinnati air samples were collected at the Continuous Air Monitoring Program (CAMP) station (Jutze and Tabor, 1963) in the downtown area. The Fairfax samples were collected in the backyard of the laboratory. Fairfax is a suburban industrial community about 9 miles from downtown Cincinnati. Fourteen 24-hour samples were collected continuously for a 2-week period in downtown Cincinnati during September 1966; three 4-day samples were collected in Fairfax during February 1967.

Andersen cascade impactor samplers (Andersen, 1966), operated about 4 feet above ground at 1 cubic foot per minute, collected and size-fractionated the particulates in six stages of inertial separation on stainless steel plates. A Type AA Millipore membrane filter, 105 mm. in diameter, was placed behind the last stage to collect unimpacted particles. Three samplers housed in a standard weather bureau shelter were operated simultaneously so that enough particulate for metal analysis could be collected in the 24-hour sampling periods.

Particulate was extracted from the collection plates by first agitating the plates in 10% nitric acid for 0.5 hour. To aid solution, the particulate was dislodged from each plate with a Teflon scraper and washed into a beaker with distilled water. Concentrated hydrochloric acid was added, and the particulate was refluxed for several hours in a final acid solution of 20% HCl and 20% HNO_3. Emission spectrographic analysis indicated that 100% of the chromium, magnesium, and cadmium, and more than 98% of the iron, copper, and lead were brought into solution by this treatment. The metal extracts were analyzed with a Perkin-Elmer 303 double-beam atomic absorption spectrophotometer with a high solids burner and an air-acetylene flame.

The size distribution of gross particulate collected with single 4-day samples in Fairfax was determined gravimetrically. The particulate was then extracted and analyzed for metals as described above.

Mass median diameters (MMD) for aerodynamically equivalent spheres of unit density were calculated for metals and total particulate by use of D_{50} stage constants—i.e., equivalent diameters at 50% mass collection efficiency—determined for the Andersen sampler by Flesch, Norris, et al. (1967) with polystyrene latex and methylene blue aerosols.

Cumulative particle-size distribution curves were obtained as in a previous study (Wagman, Lee, et al., 1967) by log-normal plots of stage D_{50} values against mass cumulative percentage data for metal or gross particulate. Values for MMD were determined by interpolation or extrapolation of the distribution curves.

Results and Discussion

Particle-size distribution curves for the six metals from samples collected in downtown Cincinnati are shown in Figure 1. For comparison, the average size distribution curve for sulfate measured at this location during the summer of 1965 (Wagman, Lee, et al., 1967) is also shown. These curves were de-

rived by numerical averaging of the 24-hour figures for cumulative per cent metal at each of the D_{50} values for the impactor stages to avoid excessive weighting of the curves for periods of relatively high metal concentration.

The composite size distribution curves for iron, lead, cadmium, chromium, magnesium, and total particulate in Fairfax are shown in Figure 2. The sulfate size distribution curve for the same location during the summer of 1965 (Wagman, Lee, *et al.*, 1967) is shown also.

The average values for metal concentrations and MMD's determined from the composite distribution curves are listed in Table I.

The size distribution curves (Figure 1) for iron, magnesium, copper, and cadmium in Cincinnati are fairly uniform in shape, with MMD values between 1.2 and 4.5 microns. The size dispersion for chromium was narrowest, with an average MMD of 1.5 microns. The size dispersion for lead was broadest, with by far the lowest MMD (by extrapolation), 0.18 micron. This value is within the range of MMD values for lead found by Robinson and Ludwig (1964) in Cincinnati and other urban areas in the United States with the Goetz centri-

Table I. Average Metal Concentration and Size Distribution

| Metal | Cincinnati, Sept. 8–23, 1966 | | Fairfax, Feb. 3–16, 1967 | |
	Concentration, µg./cu. m.	MMD, µ	Concentration, µg./cu. m.	MMD, µ
Fe	3.12	3.7	1.15	1.4
Cd	0.08	3.1	0.02	10 (est.)
Mg	7.21	4.5	0.42	7.2 (est.)
Cr	0.31	1.5	0.28	1.9
Pb	2.78	0.18 (est.)	0.69	0.42 (est.)
Cu	0.19	1.2	0.04	Not determined
Total particulate	Not measured	Not measured	44.7	1.2
SO_4	10.0	0.42 (est.)	7.2	0.42 (est.)
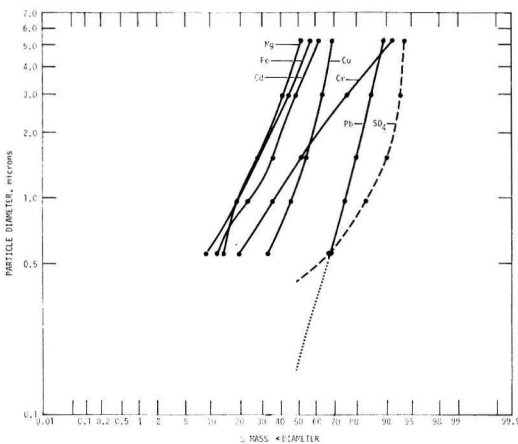
Figure 1. Cumulative particle-size distributions of various metals in Cincinnati air

Curves represent average distributions from data for 24-hour samples taken continuously for a 2-week period in the downtown area during September 1966
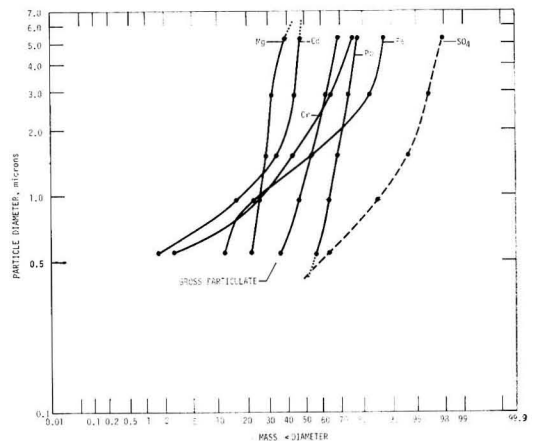
Figure 2. Cumulative particle-size distributions of various metals in Fairfax air

Curves represent average distributions from data for three 4-day samples taken during February 1967

fuge (Goetz, Stevenson, *et al.*, 1960). The size-distribution curves for these metals in Fairfax (Figure 2) differed in various degrees from the corresponding data for Cincinnati. Again, the MMD for lead was by far the lowest (0.42 micron) of the metals studied. The MMD for gross particulate in Fairfax was 1.2 microns.

A fairly extensive extrapolation required to obtain the MMD for lead in Cincinnati contributes to some uncertainty in this value. Interpolation shows, however, that about 75% of the lead in Cincinnati air was associated with particles having equivalent diameters below 1 micron. In Fairfax, these smaller particles contained about 65% of the total lead. Thus the lead in both urban and suburban atmospheres is present predominantly in particles that can penetrate and be retained in both the tracheobronchial and alveolar regions of the respiratory tract (Morrow, 1964). This finding is contrary to the conclusion by Haley (1966) that "only a small percentage of inhaled lead is in the correct particle size for pulmonary retention." Haley based his conclusion on size data by Hirschler, Gilbert, *et al.* (1957; 1964). These data were for lead in automobile exhaust gases rather than in the atmosphere; moreover, they were obtained by chemical and microscopic analysis of exhaust particulates collected in liquids, a procedure conducive to the formation of aggregates.

A comparison of the concentrations of the different metals at the two sampling locations (Table I) shows that although the chromium levels were about the same, the concentrations of iron, cadmium, lead, and copper in downtown Cincinnati were about three to five times higher than in Fairfax. Although the sampling at the two sites was not carried out simultaneously, it was nevertheless surprising to find that the average concentration of magnesium in the downtown area was about 17 times as high as that in the suburb. The high concentration of this metal in the downtown atmosphere may be attributed to a localized source since four large demolition projects carried out about three quarters of a mile west of the sampling site could have generated cement and other magnesium-containing debris.

There were no significant correlations between the metal size distributions and average humidity, day on which sampling was performed, temperature, or other environmental factors. The long sampling periods make such correlations difficult to determine. Shorter sampling periods should become feasible with improved sampling procedures and with the progressively higher sensitivities being attained by new techniques in atomic absorption spectrophotometry.

Literature Cited

Andersen, A. A., *Am. Ind. Hyg. Assoc. J.* **27**, 160–5 (1966).
Dautrebande, L., "Microaerosols," pp. 1–366, Academic Press, New York, 1962.
Flesch, J., Norris, C., Nugent, A., *Am. Ind. Hyg. Assoc. J.* **28**, 507–16 (1967).
Goetz, A., Stevenson, H. J. R., Preining, O., *J. Air Pollution Control Assoc.* **10**, 378–83 (1960).
Haley, J. H., *Arch. Environ. Health* **12**, 781–5 (1966).
Hirschler, D. A., Gilbert, L. F., *Arch. Environ. Health* **8**, 297–313 (1964).
Hirschler, D. A., Gilbert, L. F., Lamb, F. W., Niebylski, L. M., *Ind. Eng. Chem.* **49**, 1131–42 (1957).
Jutze, G. A., Tabor, E. C., *J. Air Pollution Control Assoc.* **13**, 278–81 (1963).
Middleton, W. E. K., "Vision Through the Atmosphere," University of Toronto Press, Toronto, 1952.
Morrow, P. E., *Am. Ind. Hyg. Assoc. J.* **25**, 213–36 (1964).
Robinson, E., Ludwig, F. L., "Size Distributions of Atmospheric Lead Aerosols," Final Report SRI Project No. PA-4788, Stanford Research Institute, Menlo Park, Calif., 1964.
Wagman, J., Lee, R. E., Axt, C. J., *J. Atmospheric Environ.* **1**, 479–89 (1967).

Role of Surface Acidity in the Adsorption of Organic Pollutants on the Surface of Carbon

Robert W. Coughlin and Fouad S. Ezra[1]

Department of Chemical Engineering, Whitaker Laboratory, Lehigh University, Bethlehem, Pa. 18015

■ In previous studies of adsorption on carbon, some adsorbents have displayed markedly larger adsorptive capacities than others, presumably due to differences in specific surface area as well as the nature of the carbon surface in each instance. This paper reports changes in adsorptive capacity of carbon adsorbents resulting from alteration of the carbon surface by chemical treatment, particularly with respect to formation and removal of acidic surface oxides. Increased concentration of surface oxides on carbon greatly reduces the amount of phenol and nitrobenzene that can be adsorbed from dilute aqueous solution of these compounds. In the case of phenol, adsorption from aqueous solutions of higher concentration does not appear to be strongly affected by the presence or absence of acidic chemisorbed oxygen on the surface of the carbon adsorbent. This is interpreted in terms of a two-step adsorption isotherm for phenol on carbon. Alteration of the carbon surface by oxidation and reduction appears to be reversible to a large extent, as evidenced by measurements of both surface acidity and adsorptive capacity. Possible explanations for this behavior are discussed.

B ecause of current interest in removing biologically resistant organic contaminants from waste water, considerable research has been directed toward studying the adsorption of characteristic organic pollutants on a variety of solids such as active carbon, coal, flyash, metal oxides, silicas, etc. Some of the organic compounds that can be removed from water in this way are phenols, cresols, alkylbenzenesulfonates, nitrochlorobenzenes, chlorinated paraffins, butadiene, synthetic dyes, insecticides, fungicides, etc. At present, active carbon is one of the most promising solid adsorbents for this purpose owing to its commercial availability, high adsorptive capacity, and affinity for a broad spectrum of chemical compounds.

Although numerous pertinent studies of adsorption using carbon have been reported (Dierichs and Jaehn, 1958; Joyce and Sukenik, 1962; Morris and Weber, 1962; Weber

and Morris, 1963, 1964; Kiselev, 1964; Zarifyanz, Kiselev, et al., 1967), few efforts have been directed toward learning the influence on adsorption of the nature of the carbon surface. For example, Weber and Morris studied the kinetics (1963) and equilibria (1964) for the adsorption of organic pollutants from aqueous solution onto several different kinds of carbon and found markedly different equilibrium capacities for different carbons (two to three times on a per gram basis). Although not specifically investigated by Weber and Morris, their results suggest that the differences in adsorptive capacity between one type of carbon and another may be attributable to differences in specific surface area and, perhaps, differences in the nature of the surfaces and in the kinds and populations of functional groups on the surfaces. In different but related work, Parfitt and Willis (1964) studied the adsorption of alkyl benzenes on Graphon, a graphitized carbon black having a very uniform hydrophobic surface (Cabot Corp., Boston, Mass.) and concluded that the adsorbed molecules were aligned with their major axes parallel to the adsorbent surface. However, these workers pointed out that their results differ from the findings of van der Waarden (1951) for similar systems from which the perpendicular orientation was inferred. Presumably, the difference in orientation (and, therefore, in specific adsorptive capacity) is to be attributed to the fact that van der Waarden used a carbon black with a heterogeneous surface which could cause different adsorption behavior as compared with the uniform, nonpolar surface of Graphon.

Previous experiments on the phenol-water system have shown that the phenol isotherm displays two plateaus in adsorption on carbon (Fu, Hansen, et al., 1948; Hansen, Fu, et al., 1949), whereas adsorption on a polar substrate such as alumina (Cummings, Graven, et al., 1959) leads to an s-type isotherm with a single plateau. The latter behavior has been interpreted (Giles, Mac Ewan, et al., 1960) as a monofunctional attraction toward the polar substrate arising from the hydroxyl group of the phenol. Here the phenol molecules are viewed as adsorbed end-on with larger concentrations bringing about cooperative adsorption owing to interaction of neighboring adsorbate molecules. This accounts for the s-shaped isotherm. However, in adsorption of phenol on carbon from aqueous solutions of low concentration (first plateau or step of the isotherm) the initial portion of the isotherm is not

s-shaped but appears to possess normal Langmuirian character. This suggests that the attraction of phenol for the carbon substrate lies probably in nonpolar forces operating over the entire phenol nucleus. This led Giles, Mac Ewan, *et al.* (1960) to suggest that the second step in the isotherm may represent the uncovering of a portion of the original surface of the carbon substrate by a reorientation of the phenol molecules from the prostrate to the end-on position. The approximate position of the two steps in the isotherm are consistent with surface coverage in flat orientation at the first plateau and complete coverage in vertical orientation at the second. Alternatively, the second plateau may represent a second condensed monolayer formed on top of the first.

Most commercial, adsorbent grade carbons bear chemisorbed oxygen on their surfaces and this oxygen usually takes the form of acidic sites, although chemisorbed oxygen can also exhibit basic properties. Graham (1955) studied the adsorptive capacity of Graphon and six different commercial active carbons and found that acidic chemisorbed oxygen can play a very significant role in adsorption from aqueous solution. This work revealed that acidic oxygen surface groups tend to reduce the capacity of carbon surfaces for adsorption of metanil yellow from aqueous solution whereas the adsorption of methylene blue did not appear to be materially affected. Graham attributed this behavior to a repulsive interaction between the anionic metanil yellow and the oxygen sites on the surface. He suggested that this kind of interaction might be expected for anionic adsorbates in general. These results are significant considerations with regard to the use of carbon to adsorb organic molecules from aqueous solutions, particularly in view of the face that oxidation is frequently mentioned as a means for regenerating spent or saturated carbon beds in processes of this kind. The experimental results presented below are a contribution to knowledge in this area. However, it is appropriate first to discuss the structure of carbon adsorbents and at least one model for the acidic, oxygen functional groups bound on carbon surfaces.

Structure and Chemistry of Carbon Adsorbents

Of the three known forms of carbon, diamond, graphite, and black microcrystalline carbon, only the last named form bears consideration as an adsorbent; it was at one time called amorphous carbon. There are many commercial forms of microcrystalline carbon: active carbon, carbon blacks, carbon brushes and electrodes, cokes, etc. Active carbons are frequently manufactured by carbonization of natural product carbohydrates (although coals are sometimes used as the starting material) with subsequent oxidation (activation) by gases to produce a porous structure possessing very large internal surface area. This very large specific surface area (as well as starting materials and preparation process) distinguishes active carbon from the other forms of microcrystalline carbon. Of course, active carbon frequently contains impurities, some of which are purposely added to catalyze the carbonization and oxidation steps in the manufacturing process; these impurities may affect the adsorptive power of active carbon.

The structure of microcrystalline carbon derives from graphite as was shown by Hofmann and Wilm (1936) using x-ray diffraction. It consists of graphite-like layers stacked parallel to each other in packets of some 3 to 30 layers about 10 to 100 A. thick. A graphitic layer, which may be regarded as analogous to a very large, polynuclear aromatic molecule, contains carbon atoms joined by σ bonds to three neighboring carbon atoms with the fourth electron of each atom participating in a π bond (sp^2 hybridization). In graphite, the resulting layers are stacked with a separation of about 3.35 A. in the sequence ABAB although some ABCABC sequence may also occur (Boehm and Coughlin, 1964). In microcrystalline carbon, the interlayer spacing is larger than in graphite— i.e., about 3.6 A.—and the stacking sequence is greatly perturbed with the result that many graphitic layer planes are tilted with respect to one another. The layers of both graphite and microcrystalline carbon are held together relatively weakly by van der Waals forces. In addition, there may be present in microcrystalline carbon a considerable content of disorganized tetrahedrally bonded carbon (Hofmann and Groll, 1932; Alexander and Sommer, 1956) often crosslinking different layers. Moreover, foreign atoms are always present in differing amounts, and they may be bound at the edges of the crystallites to form functional groups or incorporated within the graphitic layers to form "heterocyclic" ring systems.

Surface Functional Groups on Carbon Adsorbents

The "free valences" at the edges of the graphitic layer planes of microcrystalline carbon are very reactive and form compounds with any suitable foreign atoms present. Therefore, functional groups or surface compounds can be expected almost exclusively at the layer edges; foreign atoms or molecules can be only weakly adsorbed on the basal faces by means of the graphitic π electron system, except where they are bound at lattice defects. Most important and best known among the surface compounds of carbon are those with oxygen and sulfur, although other elements, such as chlorine and hydrogen, can also combine with elemental carbon. Of these compounds the surface oxides of carbon have received the most study, and the role of these oxides in adsorption is the principal topic of this report. In particular, the concern here is the acidic surface oxides of carbon, which are formed under the most usual conditions of treatment and manufacture of microcrystalline carbon products like active carbon. Basic surface oxides also occur, but less frequently and their nature and structure have not yet been elucidated very thoroughly. Garten, Weiss, *et al.* (1957) claim that basic oxides are produced during oxidation at high temperatures, but Boehm (1966a) has pointed out that they are formed after an outgassed carbon surface comes into contact with oxygen after cooling in an inert atmosphere.

Of the many techniques for characterizing the acidic surface oxides of carbon, the method used extensively by Boehm, Diehl, *et al.* (1964) has been employed in the present work. In an extension of earlier work (Studebaker, Huffman, *et al.*, 1956; Garten, Weiss, *et al.*, 1957) these investigators used typical identification reactions of organic chemistry to charac-
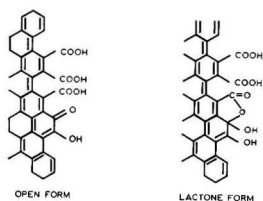
Figure 1. Possible structures of carbon surface oxides

terize oxygen chemisorbed on carbon as comprising four different types of acidic surface groups: (I) a strongly acidic carboxyl group, (II) a more weakly acidic carboxyl group, (III) a phenolic hydroxyl group, and (IV) a carbonyl group. Figure 1 shows a schematic structure representation of these groups in which the difference between the two kinds of carboxyl groups is related to their ability to form a lactone or lactol. These acidic functional groups can be identified by their reaction (or failure to react) with bases of different strength. Thus, group I is neutralized by each of the bases $NaHCO_3$, Na_2CO_3, and $NaOC_2H_5$; group II is neutralized by Na_2CO_3 or stronger bases but not by $NaHCO_3$, etc. Accordingly, simple titration with different bases serves to identify the acidic surface oxides present on a given sample of carbon.

These acidic functional groups can be produced by oxidation in air or pure oxygen or by mixing the carbon sample with aqueous solutions of oxidizing agents like $NaOCl$, $KMnO_4$, or $(NH_4)_2S_2O_8$. It is also possible to remove partially the acidic functional groups by reduction or vacuum outgassing at elevated temperatures. In addition, these groups can be made to react in other ways like esterification, formation of acid chlorides, acetylation, etc.

The general surface chemistry and the nature of functional groups on carbon and other substances has been reviewed extensively by Boehm (1966a, 1966b), and a discussion of structure and surface functional groups as they relate to active carbon has been presented by Snoeyink and Weber (1967).

Experimental

Two different microcrystalline carbons were employed in this work: an active carbon, "Columbia carbon LC325" (Union Carbide Corp., New York, N. Y.) and a pelletized

channel black, "Black Pearls 607" (P607) (Cabot Corp., Boston, Mass.). Initial preparation consisted of equilibrating for 24 hours in $0.1N$ HCl in the case of the LC325 (to remove alkaline impurities) or mere crushing in the case of the P607. All carbon samples were thoroughly washed with doubly deionized water and dried overnight at 110° C. before use in adsorption experiments. The initial treatment of LC325 with $0.1N$ HCl, followed by washing with distilled water, did not appear to cause a significant increase in base consumption upon subsequent titration; it did appear to make these titrations more reproducible, however.

The surfaces of the carbons were modified by wet oxidation and reduction. Oxidation was carried out by stirring the carbon samples in $(NH_4)_2S_2O_8$–$0.1N$ solution for 2 weeks in the case of LC325 and $0.01N$ solution for 15 to 20 hours for P607. Reduction followed by mixing the carbon and zinc amalgam, covering with concentrated HCl, and allowing to stand for 1 week. Subsequent to oxidation or reduction the carbon samples were washed and dried as described above.

The acid groups on the carbon surfaces were determined by adding excess standard base, filtering, and back-titrating with standard HCl after equilibrating for about 20 hours. In the cases of $NaOCH_2CH_3$ and NaOH, phenolphthalein was used as indicator; in the case of Na_2CO_3 and $NaHCO_3$, the indicator was methyl orange and heating was employed to drive off the CO_2 formed upon base neutralization.

Adsorption and desorption were studied by equilibrating the carbon samples at 30° C. with aqueous solutions of phenol and of nitrobenzene for about 1 week. Concentrations were measured by ultraviolet spectrophotometry at 270.0 mμ, in the case of phenol, and at 267.8 mμ, in the case of nitrobenzene. A Beckman DK-2, double-beam spectrophotometer was employed using quartz cells.

Results

The quantities of base consumed, the concentrations of functional groups (computed from quantity of base consumed), and the B.E.T. surface areas (N_2) are given in Table I for the

Table I. Surface Acidities and Surface Areas of Carbon Adsorbent Samples

Adsorbent[a]	Base Consumption, Meq./Gram				Surface Groups, Meq./Gram				B.E.T. (N_2) Specific Surface Areas, Sq. Meters/Gram
	NaOEt	NaOH	Na_2CO_3	$NaHCO_3$	I	II	III	IV	
P607	2.40	1.88	1.34	0.85	0.85	0.49	0.54	0.52	665
P607, O	3.06	2.25	1.69	0.97	0.97	0.72	0.56	0.81	668
P607, R	1.86	1.31	0.97	0.48	0.48	0.49	0.34	0.55	663
P607, OR	2.42	1.94	1.42	0.88	0.88	0.54	0.52	0.48	513
P607, OROROR	1.56	1.26	0.90	0.80	0.80	0.10	0.36	0.30	562
LC325	0.38	0.12	0.11	0.11	0.11	0	0.01	0.26	1200
LC325, O	4.15	4.22	3.10	2.20	2.20	0.90	1.12	0	556
LC325, OR	1.87	1.92	2.04	0.84	0.84	1.20	0	0	400

[a] P = Black Pearls carbon black; LC = Columbia carbon (activated); O = oxidized; R = reduced; OR = oxidation followed by reduction.

various carbon samples. Pretreatment of these samples is designated by an appended O for oxidation or R for reduction; OR means oxidation followed by reduction, etc.

Carbon samples were equilibrated with base 20 to 24 hours and the reproducibility of base consumption was within about 3 to 4%. Prolonging the equilibration time to 3 days caused only a 3% increase in base consumption. During equilibration, samples were not continuously agitated but were shaken occasionally. Continuous agitation caused a base consumption a few per cent larger than in the nonagitated cases.

The adsorption isotherms were obtained by equilibrating the samples for 1 week before analysis. When equilibration was carried out for 2 weeks, the isotherms were 8 to 10% higher than those obtained for 1-week equilibration periods, except in the case of phenol on P607 (untreated) for which there was no detectable difference.

Figure 2 presents the adsorption isotherms for phenol on the various P607 samples, and Figure 3 shows those for phenol on the LC325 samples. Figure 4 gives adsorption isotherms for nitrobenzene on two LC325 samples. Table II summarizes the plateau values for the amount adsorbed on a per gram and per unit surface area (B.E.T.-N_2) basis. Table III compares the specific surface area for the different samples as indicated by two different methods: first, as obtained by assuming the plateau of each adsorption isotherm corresponds to monolayer coverage and, second, as obtained by N_2 adsorption using the B.E.T. method. For both methods the area occupied per phenol molecule was taken as 16.1 A.² per molecule for nitrogen, 41.2 A.² per molecule for phenol, and 43.0 A.² per molecule for nitrobenzene.

Discussion

The isotherms in Figures 2 through 4, although covering ranges of very low composition, appear to be of the Type I, or Langmuir, variety. The plateaus of these isotherms suggest surface coverage of the adsorbent in the range of 5 to 40%, well below the monolayer region. This is in agreement with the work of Weber and Morris (1964), who observed that the phenol isotherm exhibits similar shape at high and at low concentrations; in their work, the curvature observed from data covering low concentration was completely concealed when plotted with data obtained at high concentrations owing to compression within the first few divisions on the scale of concentration. They argued this sort of continuous curvature suggests multilayer adsorption with a range of activities for various portions of the adsorbent surface. A similar kind of argument has been invoked by Hansen, Fu, *et al.* (1949), who found the number of adsorbed layers at saturation to be on the order of three or four for alcohols possessing four or more carbon atoms.

In Table I, neither the equilibrium consumption of the various bases, nor the concentrations of the various surface functional groups deduced therefrom, seem to indicate any interrelationship as was reported by Boehm, Diehl, *et al.* (1964). This could be attributed solely to nonuniformity of
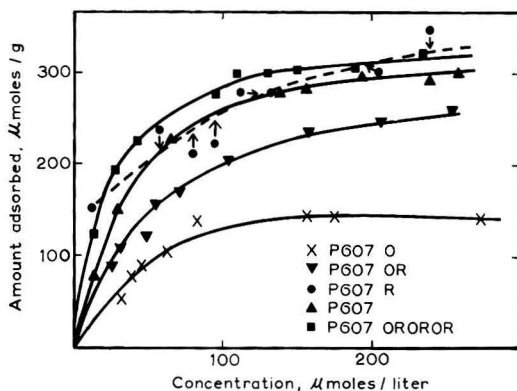
Figure 2. Adsorption isotherms of phenol on Black Pearls 607 carbon black from aqueous solution

30° C., 1 week equilibrium time
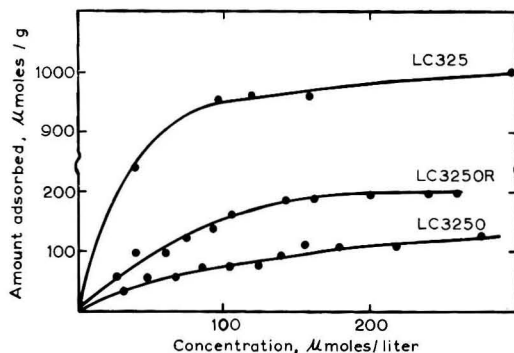
Figure 3. Adsorption isotherms of phenol on activated Columbia carbon LC325 from aqueous solution

30° C., 1 week equilibrium time
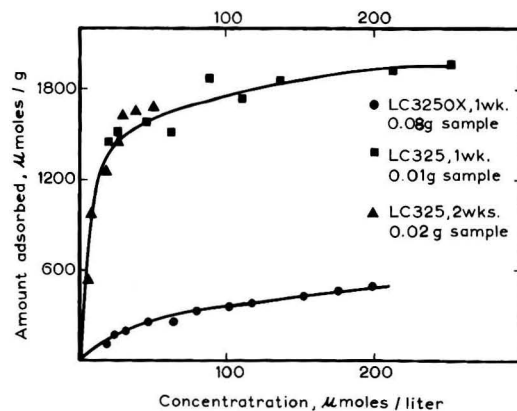
Figure 4. Adsorption isotherms of nitrobenzene on activated Columbia carbon LC325 from aqueous solution, 30° C.

Table II. Plateau Values for the Adsorption of Phenol and Nitrobenzene

Adsorbent	Phenol Adsorption		Nitrobenzene Adsorption	
	μmoles/g.	μmoles/ sq. meter	μmoles/g.	μmoles/ sq. meter
P607	290	0.478		
P607, O	142	0.213		
P607, R	330	0.498		
P607, OR	250	0.488		
P607, OROROR	312	0.555		
LC325	1000	0.833	1950	1.63
LC325, O	120	0.216	500	0.90
LC325, OR	190	0.475		

Table III. Surface Area of Carbon Samples

	Surface Area, Sq. Meters/Gram		
Adsorbent	Isotherm plateau for phenol	Isotherm plateau for nitro-benzene	B.E.T. (N_2)
P607	73.5		655
P607, O	34.8		668
P607, R	87.–89.0		663
P607, OR	62.0		513
P607, OROROR	77.3		562
LC325	268.0	504	1200
LC325, O	29.8	196	556
LC325, OR	48.7		400

oxidation and reduction treatments both with respect to reagents and treatment time in the work reported here. However, there are striking differences between the base consumptions by carbon of different treatment histories. Table I clearly shows that reduction markedly decreases surface acidity, whereas oxidation causes the surface concentration of acid groups to increase significantly.

The effects of oxidation and reduction on the different functional groups appear not always to be similar in degree for all adsorbents, although the general trend is clearly evident from the data in Table I. In particular, the untreated active carbon LC325 appears to possess a substantially smaller quantity of surface acidity when compared with the untreated Black Pearls 607. Upon oxidation, the LC325 develops a rather large amount of surface acidity, and its original low acidity is not nearly restored by subsequent reduction. This is in contrast to the oxidized P607, which appears to be returned to almost its original acidity by reduction.

The approximate locations of the apparent plateaus of the various isotherms have been estimated visually, and these values have been assembled in Table II for the purpose of comparison. These "plateau values" represent the adsorption capacities of the various carbons at the concentrations employed. Here, these quantities are expressed in two ways: μmoles adsorbed per gram of adsorbent and μmoles adsorbed per square meter surface area of adsorbent; the latter quantities were computed by using the values of specific surface area obtained from N_2 adsorption by the B.E.T. method. Whether the adsorptive capacities of the carbons given in Table II be compared on a per gram or per unit surface area basis, it is clear that the acid groups on the surface resulting from oxidation appear to have a significant effect on adsorption. In particular, the oxidized sample of P607 manifests adsorptive capacities for phenol about half those displayed by the reduced samples.

In the case of the active carbon, LC325, the effect of oxidation appears to be even more pronounced. Oxidation reduces
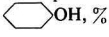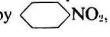
the adsorptive capacity of this carbon for phenol by a factor of about eight on a per gram basis or by a factor of about four on the basis of unit surface area. For the adsorption of nitrobenzene on this carbon the effect of oxidation on adsorptive capacity is somewhat smaller: a decrease by a factor of about four on a per gram basis or by a factor of about two on a unit surface area basis.

Examination of the B.E.T. (N_2) surface areas for the adsorbent samples shows little material change upon oxidation and reduction treatment for the P607, whereas these treatments reduce the specific surface area of LC325 by a factor of two to three. Presumably this difference results from the less severe oxidation conditions to which the channel black was subjected. However, it may also be closely connected with the complex structure of very fine pores in an active carbon compared with what is probably a more open network of larger pores in the case of the carbon black. The more delicate network of pores in an active carbon might be expected to suffer a more drastic decrease in surface area upon oxidation. The data in Table I also suggest that reduction of oxidized samples brings about small decreases in specific surface area. Reduction with hydrogen might be expected to split off parts of the oxygenated carbon structure, although experimental conditions were not those that usually favor hydrogenolysis. Capillary condensation of low molecular weight products of oxidation and reduction is another possible partial explanation for the observed losses in surface area.

Table IV lists the percentages of total adsorbent surface area (taken as the B.E.T.-N_2 measurement) which is occupied by adsorbate in the plateau region. The adsorptive capacities of the carbons, expressed in this way, also display the strong effects of treatment by oxidation or reduction. There is good correlation between total acidity ($NaOCH_2CH_3$ consumption) and the percentage of adsorbent surface covered by phenol (Figure 5). Similar correlations exist between the adsorptive capacities and the concentrations of weaker acidic sites on the surface but, in the latter instances, there appears to be a

Table IV. Percentage of Adsorbent Surface Area (B.E.T.-N₂) Occupied by Phenol and by Nitrobenzene

Adsorbent	Surface Occupied by ⬡OH, %	Surface Occupied by ⬡NO₂, %
P607	11.2	
P607, O	5.2	
P607, R	13.2	
P607, OR	12.1	
P607, OROROR	13.8	
LC325	22.3	42.1
LC325, O	5.4	35.2
LC325, OR	12.2	
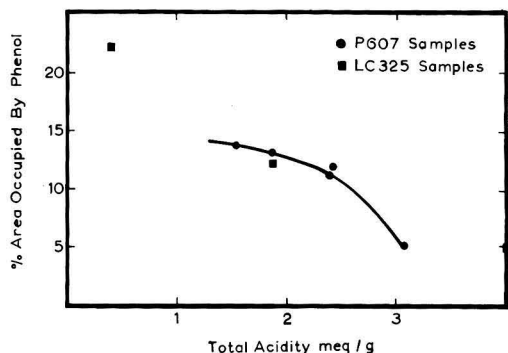
Figure 5. Per cent area occupied by phenol *vs.* total amount of acidity

lesser dependence and the data scatter more. It is not yet possible to assess the possibly different degrees to which the different groups influence the adsorptive capacity. Research into the problem is continuing.

Dependence of adsorption on the nature of the carbon adsorbent surface has been reported before (Parfitt and Willis, 1964; Graham, 1955; Clauss, Boehm, *et al.*, 1957; Zettlemoyer and Narayan, 1966; Kipling and Gasser, 1960), but the present authors are not aware of any work in which the same carbon has had its adsorptive capacity lessened and subsequently regenerated by chemical treatment. In fact, from the data reported here, the treatment of carbon black seems to be reversible through up to three cycles of oxidation and reduction, at least in so far as the phenomenon of phenol adsorption is concerned. This work is currently being extended to other adsorbates and greater numbers of oxidation and reduction cycles.

Most previous work reported about adsorption onto carbon surfaces has not concerned aqueous solutions. Perhaps the two papers most relevant to the present work are those by Graham (1955) and Clauss, Boehm, *et al.* (1957). Graham (1955) used six different active carbons and a graphitized carbon black (Graphon) and found that acid groups on the carbon surface tend to reduce the capacity for adsorption of metanil yellow (an anion) from aqueous solution although not for adsorption of methylene blue (a cation), which has about the same size molecule. On the other hand, Clauss, Boehm, *et al.* (1957) showed that a B.E.T. analysis of phenol adsorption data from aqueous solution on several different carbon blacks treated in different ways resulted in values of specific surface area in substantial agreement with those obtained by B.E.T. (N₂) adsorption. In this case then, phenol adsorption from aqueous solution did not appear to be affected by acidic surface groups in different concentrations on the carbons (as a result of graphitizing, outgassing at high temperature, activation, etc.). The apparent lack of agreement between these results and the present work can be attributed to the high phenol concentrations used by Clauss and coworkers. This means that much of their data fell in the multilayer region of surface coverage, whereas the results reported here pertain to coverages well below the monolayer region. The present results, obtained at the low aqueous phenol concentrations of interest from the standpoint of water treatment, are a more sensitive measure of the interaction between the phenol solution and the carbon surface in contrast to the work of Clauss, Boehm, *et al.* (1957).

The difference between the role of the carbon surface in adsorption equilibrium at low phenol concentrations as compared with large concentrations is illustrated by Figure 6. Here some additional data for phenol adsorption on carbon at high concentrations are plotted with the data discussed above. The steps or plateaus evident in the phenol isotherms of Figure 6 would not appear so well defined had a continuous concentration range been plotted. A uniform scale would tend to compress the isotherms so that what appear as steps in Figure 6 might seem more like continual increases. Figure 6 clearly shows that the chemically bound oxygen on the carbon adsorbents appears to influence the position of the first plateau of the phenol isotherm but not the second or high concentration plateau. Thus, oxygen chemisorbed on carbon appears to influence strongly phenol adsorption only under conditions when the molecules are thought to be adsorbed in the prone position on the graphitic basal planes with attractive forces operating over the entire phenol nucleus. This oxygen appears to exert very little influence on phenol adsorption under conditions where the molecules are thought to be adsorbed in the vertical or end-on position with forces of interaction between phenol molecules themselves presumably affecting the process more than forces between the phenol and the substrate.

Possible explanations for the role of the acidic surface oxygen groups in inhibiting adsorption of phenol and nitrobenzene molecules from aqueous solution are interesting to consider. The major portion of these oxygen groups on carbon are presumably located at the edges of the layer planes where they would not be expected to interfere markedly, in a steric sense, with adsorption of organic molecules onto the basal planes. Oxygen chemically bound on the edges can localize electrons in surface states thereby removing them from the π electron system of the basal planes. Walker, Austin, *et al.* (1965) have explained the effect of oxygen chemisorption on the thermoelectric power of carbon by similar reasoning. Increases in thermoelectric power of carbon owing to oxygen chemisorption were attributed by these workers to a depletion
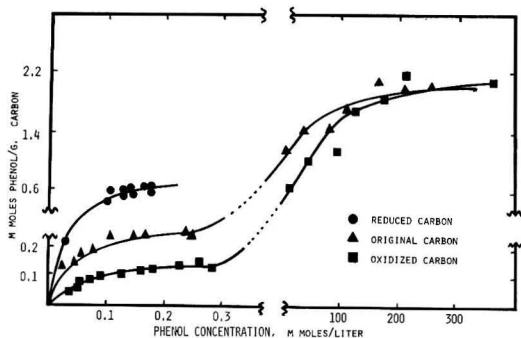
Figure 6. Adsorption of phenol on Black Pearls 607 carbon black from aqueous solutions, 30° C.

in the number of electrons and an increase in the population of positive holes in the conduction band of the π electron system. These considerations appear consistent with the concept of dispersion forces between the phenol π electron system and the π band of the graphitic planes of the carbon as responsible for adsorption. Removal of electrons from the π band of the carbon by chemisorbed oxygen might be expected to interfere with and weaken these forces.

Another phenomenon that could be expected to play a role in the adsorption studies reported here is the bonding of water molecules to the oxide functional groups. According to Dubinin (1966), the water molecules adsorbed to the oxygen groups become secondary adsorption centers which retain other water molecules by means of hydrogen bonds. As a result, complexes of associated water form within the pores of a carbon adsorbent. These complexes could prevent the migration of organic molecules to a large portion of the active surface area within a particle of adsorbent. However, if this were the case, the chemisorbed oxygen would be expected to exert an influence on the second phenol adsorption plateau similar to that evident for the first plateau. Another possible explanation of the observed phenomena may reside in a model based on capillary condensation in which the low concentration part of the isotherm is affected by oxygen complexes in the micropores, whereas condensation at higher concentration in the larger pores might not be so affected. The evidence for any single explanation is not overwhelming, however, and it is hoped that continuing research will shed more light on this question.

The work presented above shows that chemical treatment of a carbon surface can strongly alter its adsorptive capacity and that these effects are due to more than mere changes in surface area. These results for the effects of chemisorbed oxygen are significant in view of the fact that regeneration of carbon adsorbents frequently involves some degree of oxidation. The addition of a reduction step to the regeneration process would appear to have the obvious technical advantage of increased adsorptive capacity for nitrobenzene and phenol at low concentrations. Further, in the manufacture of adsorptive carbon, control of chemical and physical process conditions might be harnessed to produce carbon surfaces suitable for particular adsorption applications.

Literature Cited

Alexander, L. E., Sommer, E. C., J. Phys. Chem. 60, 1646 (1956).
Boehm, H. P., Advan. Catalysis 16, 179–274 (1966a).
Boehm, H. P., Angew. Chem. Intern. Ed. Engl. 5 (6), 533–44 (1966b).
Boehm, H. P., Coughlin, R. W., Carbon 2, 1 (1964).
Boehm, H. P., Diehl, E., Heck, W., Sappok, R., Angew. Chem. Intern. Ed. Engl. 3 (10), 669–77 (1964).
Clauss, A., Boehm, H. P., Homfann, U., Z. Anorg. Allgem. Chem. 290, 35–51 (1957).
Cummings, T., Graven, H. C., Giles, G. H., Rahman, S. M. K., Snedden, J. G., Stewart, C. E., J. Chem. Soc. 1959, p. 535.
Dierichs, A., Jaehn, L., Chem. Tech. (Berlin) 10, 567 (1958).
Dubinin, M. M., in "Chemistry and Physics of Carbon," P. L. Walker, Jr., Ed., Vol. 2, p. 51, Marcel Dekker, New York, 1966.
Fu, Y., Hansen, R. S., Bartell, F. E., J. Phys. Colloid Chem. 52, 374 (1948).
Garten, V. A., Weiss, D. E., Willis, J. B., Australian J. Chem. 10, 295 (1957).
Giles, C. H., Mac Ewan, T. H., Nakhwa, S. N., Smith, D., J. Chem. Soc. 1960, p. 3973.
Graham, D., J. Phys. Chem. 59, 896 (1955).
Hansen, R. S., Fu, Y., Bartell, F. E., J. Phys. Chem. 53, 769 (1949).
Hofmann, U., Groll, E., Ber. 65, 1257 (1932).
Hofmann, U., Wilm, D., Z. Elektrochem. Angew. Physik. Chem. 42, 504 (1936).
Joyce, R., Sukenik, V. A., Advan. Waste Treatment Res., U. S. Public Health Service, Cincinnati, Ohio, May 15, 1962.
Kipling, J. J., Gasser, C. G., J. Phys. Chem. 64, 710 (1960).
Kiselev, A. V., Rev. Gen. Caoutchouc. 41, 377 (1964).
Morris, J. C., Weber, W. J., Proc. Intern. Conf. Water Pollution Res. 1st, Pergamon Press, Oxford, England, 1962.
Parfitt, G. D., Willis, E., J. Phys. Chem. 68 (7), 1780 (1964).
Snoeyink, V. L., Weber, W. J., ENVIRON. SCI. TECHNOL. 1 (3), 228–34 (1967).
Studebaker, M. L., Huffman, K. W. D., Wolfe, A. C., Nabors, L. G., Ind. Eng. Chem. 48, 162 (1956).
Waarden, M. van der, J. Colloid Sci. 6, 443 (1951).
Walker, P. L., Jr., Austin, L. G., Tietjen, J. J., in "Chemistry and Physics of Carbon," P. L. Walker, Jr., Ed., Vol. 1, p. 328, Marcel Dekker, New York, 1965.
Weber, W. J., Morris, J. C., J. Sanit. Eng. Div., Am. Soc. Civil Engrs. 89 (SA2), 31 (1963).
Weber, W. J., Morris, J. C., J. Sanit. Eng. Div., Am. Soc. Civil Engrs. 90 (SA3), 79 (1964).
Zarifyanz, Y. A., Kiselev, V. F., Lezhnev, N. N., Nikitina, O. V., Carbon 5, 127–35 (1967).
Zettlemoyer, A. C., Narayan, K. S., in "Chemistry and Physics of Carbon," P. L. Walker, Jr., Ed., Vol. 2, p. 197, Marcel Dekker, New York, 1966.

Water Sample Filtration Unit

Marvin W. Skougstad and George F. Scarbro, Jr.

U. S. Geological Survey, Denver, Colo. 80225

■ A readily portable, all plastic, pressure filtration unit is described which greatly facilitates rapid micropore membrane field filtration of up to several liters of water with a minimum risk of inorganic chemical alteration or contamination of the sample. The unit accommodates standard 10.2-cm. (4-inch) diameter filters. The storage and carrying case serves as a convenient filter stand for both field and laboratory use.

Reported chemical-quality characteristics of water samples normally include only those substances which are in solution at the time of analysis. This implies that all suspended particulate matter has been removed from that portion of the sample from which aliquots for analysis are taken. Turbid samples obviously require a preliminary separation of the suspended material. Many apparently clear samples, however, may contain a surprising amount of filterable material. Questions may arise as to the certainty of removal of particulate matter prior to analysis and, equally important, as to the criteria used to distinguish particulate material from substances in true solution. While these questions may be of little significance when only the major constituents are determined, they are of real concern when the sample is analyzed for minor or trace constituents. A small amount of finely dispersed particulate material may contribute the greater part of the total determined amount of a given trace constituent.

The removal of suspended solids may be accomplished by any one of a number of techniques, and there is presently little uniformity among water analysis laboratories as to the method used. Slow settling, centrifuging, and filtration are all commonly used. Within recent years, however, micropore membrane filters of controlled, uniform pore size and consistent high quality have become commonplace in most analytical laboratories. As a consequence, many analysts now remove suspended particulate matter from water samples by filtration through micropore membrane filters having an average pore diameter of 0.45 micron. Such practice, indeed, has much to recommend it. The accurate control of pore sizes in the membrane material assures consistently reproducible removal of particulate matter from the sample. Filtration

rates are reasonably good because of the high ratio of pore area to total filter area. Although the membrane filters are somewhat fragile, they are sufficiently durable so that, with reasonable care, they can be easily handled. The choice of a membrane filter of an average pore diameter of 0.45 micron permits a reasonable and practical distinction between true solute material and material that may be considered particulate or not in true solution.

From the foregoing, one can infer the desirability of establishing a standard water sample filtration procedure using a micropore membrane filter of 0.45-micron average pore size. If a standard procedure were followed, the users of water-quality data could be assured that exactly comparable samples had been analyzed by all laboratories.

One additional important factor must be considered. In the process of collecting and analyzing a water sample, significant chemical changes in the sample may occur during the time interval between collection of the sample and its later analysis in the laboratory. Such changes may involve both an increase in the amount of dissolved material, as occurs when finely divided solids are slowly dissolved by the solvent or solution, and a decrease in dissolved material, as when precipitation occurs. For this reason, it is desirable to filter each sample at the time it is collected. If this is done, any solids which have appeared in the sample by the time the analysis is begun can only be concluded to have not been present as such in the original sample. Such material must have been in solution at the time of collection and, therefore, should be included in the analysis and be reported as a part of the total solute concentration of the original sample. Depending upon the determinations to be made, any such solids may be either redissolved or uniformly dispersed throughout the sample before sample aliquots are withdrawn for analysis.

Immediate filtration of the sample at the time of collection also eliminates, or at least greatly minimizes, chemical and solvent action between solution and solids.

Hence, it would seem desirable to standardize not only the filtration technique for removal of particulate matter from water samples prior to analysis, but also the entire sample collection operation, even to the extent that the filtration be performed immediately at the time the sample is collected. Admittedly, even such a procedure has limitations. It does, however, eliminate many of the uncertainties encountered in

any attempt to provide a water sample which reliably represents conditions at the time of collection.

Field Filtration

Heretofore, micropore membrane field filtration of the several liters of water frequently needed for a complete chemical analysis has been neither a convenient nor a simple operation. The usual glass micropore–filter funnel and suction flask arrangement accommodates only a comparatively small-diameter filter disk, making the filtration of large volumes, particularly of turbid samples, a tedious and slow process. Glass apparatus items are easily broken when used in the field, and metal funnels and holders cannot be used when minor constituents are determined because of the possibility of contamination of the sample. Even stainless steel and monel may contribute detectable amounts of metallic contaminants. Finally, vacuum filtration is neither efficient nor practical when the operation must be accomplished in the field away from a good vacuum supply. A pressure filter can be more easily operated in the field and is much more effective.

This report describes the design and use of a portable all-plastic pressure filter which is uniquely suitable for the field filtration of up to several liters of water. Since it is constructed entirely of inert materials, there is a minimum risk of inorganic contamination or alteration of the sample. It is lightweight and therefore readily portable. Moreover, it is strong and durable and is not easily damaged or broken, even under hard field use. Filtration pressures up to 65 pounds (p.s.i.g.) can be applied with adequate margin of safety. The unit accepts a standard 10.2-cm. (4-inch) diameter filter disk, and although designed especially for micropore membrane filters, any similar material can be used. A filter of this diameter permits reasonably rapid filtration of all but the most turbid samples and is a compromise between a larger diameter filter, which would speed the filtration of turbid samples but would also be more costly and would necessitate a heavier, more bulky apparatus, and a smaller diameter filter, which would lack the necessary capacity to handle large volumes.

Description

The filter unit (Figure 1) consists of three separable sections: a bottom flange and filter support, *A*, a sample reservoir, *B*, and a cover, *C*. When assembled and fastened with nylon
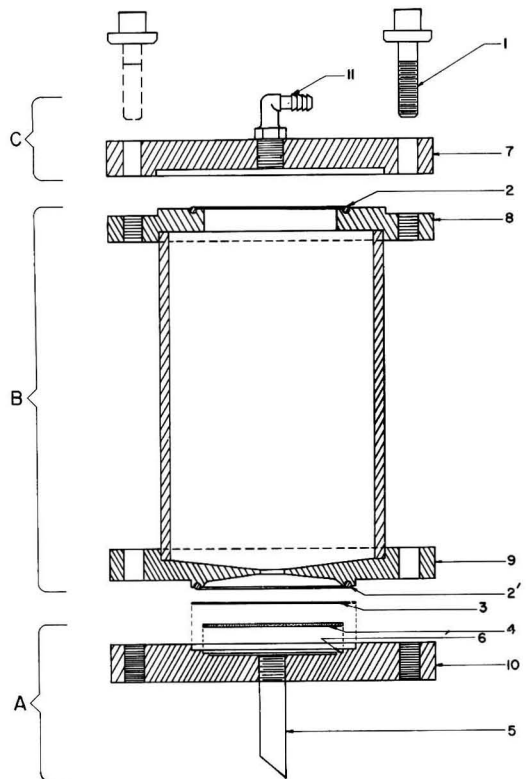
Figure 1. Pressure filter—parts and construction

thumb screws, *1*, the two silicone O-rings, *2, 2'*, provide a pressure-tight seal. The micropore membrane filter, *3*, is supported on a porous polyethylene disk, *4*, set in a recess, *6*, cut in the bottom flange section, *10*. This disk must fit with perfect smoothness into its recess in the flange to provide an even, uniform surface for the support of the membrane filter. Any irregularity will cause rupture of a wet membrane filter when pressure is later applied.

The drain stem, *5*, is a short length of polyvinyl chloride pipe, cut and threaded into the bottom flange section, *10*.

The sample reservoir, *B*, consists of a section of a lucite cylinder of 6.4-mm. ($^1/_4$-inch) wall thickness cemented into shallow recesses cut into the upper, *8*, and lower, *9*, lucite flanges. The reservoir (12.5-cm. I.D. $\times$ 20.5 cm. long) has a capacity of about 2.5 liters—ample for the collection of a filtered 2-liter sample with a liberal allowance for prerinsing of both the apparatus and the collection bottle. The dimensions of the reservoir may be adjusted according to individual needs or preference, although probably very little would be gained, for most applications, by any considerable deviation from the dimensions given here.

Note that the inner surface of the lower flange, *9*, of the reservoir is tapered to a 1.9-cm. ($^3/_4$-inch) hole in its center. This permits complete drainage of the sample from the reservoir and, more important, provides a protective baffle which prevents damage to the fragile filter disk when sample is poured into the reservoir. The underside of this flange is also tapered toward the center hole to facilitate escape of air bubbles trapped above the filter disk.

A removable lucite flange, *7*, is provided to simplify the addition of sample and for ready access to the reservoir for cleaning. A suitable length of rubber pressure tubing is attached at the polyvinyl chloride hose-connector fitting, *11*, and an ordinary automobile tire valve is sealed into the opposite end of the pressure tubing to permit easy attachment of a pressure pump. The tire valve also serves as a necessary pressure release valve for relieving the interior pressure before disassembling the unit or removing its cover. Only thoroughly cleaned pressure tubing should be used to avoid contamination of the sample. A small air pump, such as is used to inflate volleyballs, will provide adequate pressure for rapid filtration of most samples. Moreover, its small, handy size makes it particularly suited for field use since it can be fitted into the filter carrying case along with the filter unit. When an athletic air pump is used, a short length of adapter hose containing a a screw fitting for attachment to the tire valve must be provided.

Alternatively a regular or heavy-duty automobile tire pump may be used to obtain the necessary filtration pressure. Whereas the athletic air pump easily produces a working pressure of 40 to 50 pounds (p.s.i.g.), a tire pump will provide up to about 65 pounds (p.s.i.g.). The filtration unit may be operated at pressures up to 85 pounds (p.s.i.g.) with complete safety. Because the maximum pressure that can be obtained even with a heavy duty tire pump is less than 85 pounds, the operator is always assured of safe operation. Hence, when the filter unit is used normally in this manner, a safety valve or pressure gage is unnecessary. Incorporating these items would only make the simple unit unduly complex and would significantly increase its construction cost. Indeed, a pressure gage would be intolerable if attached to the unit itself, because of the sample contamination that would certainly result. A word of caution is necessary, however: Whenever the filter is operated from any pressure source that may exceed 85 pounds (p.s.i.g.), such as from a cylinder of compressed air or nitrogen, or from a high pressure air line, it is absolutely essential that adequate precautions are taken to make certain that safe operating pressures are never exceeded. Normally, this requires that a pressure regulator and a pressure indicating gage be installed ahead of the filter unit.

In actual practice, working pressures in excess of 65 pounds (p.s.i.g.) are of no advantage when filtering turbid samples. Once the filter membrane becomes caked with accumulated residue and the filtration rate becomes excessively slow, a further increase in pressure only compresses the filter cake and further restricts the flow of filtrate. At this point it is best to interrupt the filtration and replace the filter disk with a new one.

Operation

The carrying case (Figures 2 and 3) protects the filter unit when not in use and serves also as a convenient filter stand for field filtrations. When the case is placed on end and the plastic plug, *12*, is removed from the top opening, *13*, the filter unit may be placed firmly on the case with its drain stem, *5*, extending through the opening in the case and into the neck of a sample-collection bottle. A sliding shelf, *15*, may be inserted into any one of three positioning slots, *14*, to accommodate 1-, 2-, or 4-liter, narrow-mouthed polyethylene bottles.

Use of the pressure filter is straightforward. Careful attention to a few details, however, will ensure satisfactory operation and filtration. The low wet strength of membrane filters makes them susceptible to tearing during assembly of the unit. For this reason, it is essential that the polyethylene filter disk support, *4*, the entire bottom flange section, *10*, and the O-ring, *2*, be thoroughly dry when a membrane filter is placed in position. Drying of these parts may best be accomplished by wiping and blotting with a clean towel or absorbent tissue.

The unit can be assembled and a pressure-tight seal achieved by drawing the six nylon thumb screws to finger tightness. The three screws on each of the upper, *7*, and lower, *9*, flanges should be tightened evenly and firmly to avoid undue strain and distortion and to ensure uniform pressure on the O-ring seals. Forceful tightening of the thumb screws is not
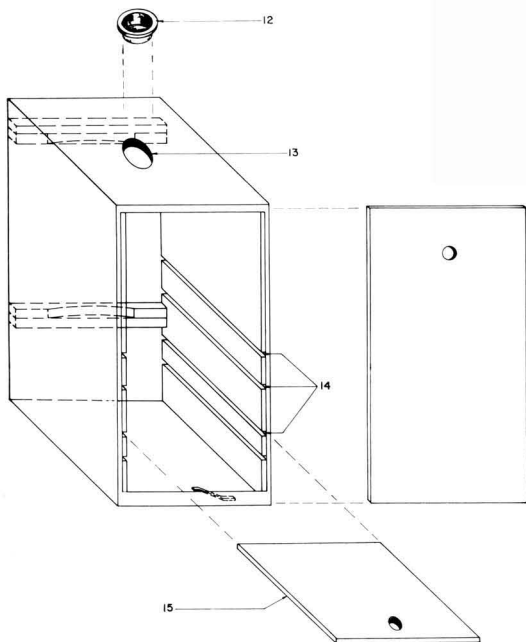
Figure 2. Storage and carrying case

Figure 3. Field filtration

necessary and should be avoided. Since the seals are readily visible through the clear plastic flanges, a quick inspection indicates whether or not the O-rings are uniformly sealed. Disassembly of the unit or removal of the cover is best accomplished after the air pump has been disconnected and the pressure inside the unit has been released.

The authors recommend that the first three 50- to 75-ml. portions of filtrate be discarded, using them only to rinse a newly installed filter, the filter funnel itself, and the receiving bottle. It is desirable, whenever possible, to rinse the reservoir with one or two portions of the sample before filling it with the solution to be filtered. With these precautions and by thoroughly rinsing the apparatus before beginning the collection of a filtered portion of a sample, the possibilities of sample contamination are greatly minimized.

Lucite is a moderately soft plastic material and is easily scratched. Therefore, reasonable care should be used in handling and cleaning the filter unit. Abrasive cleaners should not be used, and all sediment residues should be removed immediately by flushing and thorough rinsing. Organic solvents which attack the plastic should, of course, be avoided. Mild detergent solutions or dilute mineral acids may be used without damage to the filter unit. With proper treatment, the unit will give long and satisfactory service.

Performance

A 0.45-micron average pore diameter membrane filter effectively removes particulate matter of dimensions exceeding 0.45 micron. Indeed, many smaller particles are either trapped within the interstices of the membrane, held to the membrane by electrostatic forces, or retained on the surface as the residue accumulates. The over-all range of sizes of particulate matter removed depends on the amount and the nature of the suspended material present, and there can be no sharp distinction between the size of particles retained and passed. Although no significant amount of material greater than 0.45 micron appears in the filtrate, at least some material of smaller size is also removed.

Field filtration rates using the pressure filter are at least 10 times faster than those obtained with a suction filter operated from either a hand pump or an automobile exhaust manifold. In many cases, use of the pressure filter makes practical the field filtration of samples which otherwise would require an unreasonably long filtration time. As an example, one 200-ml. sample which required more than 2 hours to filter by suction filtration was filtered in less than 10 minutes using the pressure filter and a hand pump. When field filtration is necessary, it is estimated that a savings of at least 50% in sample collection costs are realized.

BOOKSHELF

Compleat aqueous waste control guide

Aqueous Wastes from Petroleum and Petrochemical Plants. Milton R. Beychok. ix + 370 pages. John Wiley & Sons, Inc., New York, N.Y. 10016. 1967. $12.75, hard cover. *Nelson L. Nemerow is professor of civil engineering, Syracuse University.*

By Nelson L. Nemerow

The objective of the book is to provide design data for oil waste treatment. Beychok seems to present just enough know-how for the industrial designer of petrochemical plants. In the introductory material I question the validity of COD lower than BOD for domestic sewage (page 13).

The author provides useful data on effluent quality regulations for Sweden, Australia, South Africa, England, and several states in the U.S. for swimming, fishing, and industrial waste (Table 1, page 18). He continually deplores lack of complete information in other published papers and sources. However, he presents very clear and well defined descriptions of waste sources and types.

The author describes carefully and extensively various segregation systems and makes rather specific recommendations for the selection of a system. He does not attempt to describe oil refining to the generalist, consulting engineer, or student, but only describes in detail various processes and wastes with a view toward treatment. He presumes extensive reader knowledge of the petrochemical industry and little knowledge of waste treatment. The author feels that existing literature —including his own text—lacks sufficient "definitive data concerning specific effluents from specific processes."

Beychok goes into considerable depth and detail on fundamentals concerning some wastes such as H_2S in sour condensates (Figure 7, page 53). Although the objective as stated is to assist the process engineer in designing, one wonders how capable the engineer is in assimilating and integrating the theories presented. The material may be even more useful for researchers.

The author includes a helpful system of summarizing information within a chapter to aid the reader in evaluating what has been presented thus far (a useful example is on page 71).

About half of the book is devoted to theoretical formulation, tables, graphs, and calculations to assist the engineer in predicting compositions and quantities of contaminants in various wastes. The remainder of the book, or at least Chapter 3, is devoted to waste treatment methods. This subject is the heart of the text as far as the industrial waste engineer is concerned. The author splits this chapter into three main sections:

• In-plant pretreatment.
• API and similar separators.
• Secondary treatment following API separator.

In Chapter 3, the author describes and discusses most of the more common treatment methods. He also develops some typical process design methods. Design procedures are included for sour water strippers, spent caustic oxidizers, spent caustic neutralizers, API oil-water separators, and oxidation ponds. Several secondary treatment units are described and discussed, including chemical coagulation, activated sludge processes, trickle filter processes, and Pasveer-Sloot oxidation ditches. Beychok also presents information on air flotation, aeration basins, and biological oxidation in cooling water towers.

Beychok devotes most of Chapter 3 to theory and mathematical analyses for design details. When it is necessary to install secondary treatment (remembering that the author uses this term to describe any treatment following API separators), typical complete waste treatment facilities may include:

• In-plant segregation and pretreatment.
• Storm water surge pond.
• API oil-water separation.
• Air flotation or chemical coagulation (for further removal of oil and suspended solids).
• Biological oxidation.

• Sludge dewatering and disposal (probably by incineration).

• Perhaps a final holding basin.

• Special facilities for special hazardous or toxic wastes.

The author gives a great deal of attention to specific design details. For example (14, page 211), he describes the design of a sulfide oxidation unit.

Dearth of data

The author deplores the lack of performance data on API separators, even though there has been a great deal of material written about them, including the API Manual. He provides, from the literature (Table 24, page 226), data showing percentage removals of oil from 52–60%. No separators reported in the literature yielded effluents with less than 20 p.p.m. oil.

The book contains an Appendix 8, which is reprinted from the "European Chemical News" of Nov. 11, 1965, a Pollution Supplement, devoted wholly to the listing and discussion of national and international pollution regulatory organizations and legislation.

He provides a unique chapter on cost data which is useful but only of ball park range. By the author's own admission, the values may exhibit a variation of as much as 4 to 1 in cost. Discussion on cost is brief (five pages).

The author presents an interesting, helpful, and novel method of referencing material at the end of the book where references are in five sections:

• General.

• Refinery and petrochemical plant effluents.

• Spent caustic and foul water.

• Physical and chemical data.

• Miscellaneous.

He also provides in the index a special section devoted to his examples. This is helpful to the reader wishing only to locate quickly the author's example design, such as the API oil-water separator.

This book should be in the libraries of all waste engineers, even if they are not directly associated with the petrochemical industry. The author obviously spent many years collecting this information and putting it into such a useful form. He has made a valuable contribution to our field and deserves our thanks for his hard work and tireless effort.

NEW PRODUCTS DIGEST

Synthetic cationic coagulant effective for water treatment

A synthetic, organic, cationic polyelectrolyte coagulant for use in potable water treatment, Cat-Floc may be used as a primary coagulant in place of alum or iron salts or as a coagulant aid in conjunction with conventional treatment chemicals. The manufacturer notes that use of Cat-Floc as a primary coagulant eliminates carryover of iron and aluminum, which foul zeolite softeners.

As a primary coagulant, use levels range from 0.2 to 7.0 p.p.m., and as a coagulant aid, from 0.15 to 2.0 p.p.m. According to the company, the product is equally effective in clarifying industrial process water and waste water. Bulletin 12-24A states that Cat-Floc produces faster-forming, faster-settling, more filterable floc, and that it reduces chemical costs and storage and handling costs.

The company has demonstrated the effectiveness of the product in jar tests (above) on water from the Ohio River following moderate run-off. Water in all three beakers was agitated for 15 minutes at decreasing speeds, following treatment with Cat-Floc and clay. After 2 minutes' settling, the beakers show appreciably clearer water in the jar on the right (with Cat-Floc and a clay) than in the jar in the middle (treated only with clay) or the jar on the left (untreated river water). Calgon Corp. **61**

Ion-Exchange Membrane Filters

Acropor Type SA and Type SB membrane filters permit high recovery of trace quantities of cations or anions in very dilute solutions. Acropor-SA is a strong acid ion-exchange membrane, while Acropor SB is a strong base ion-exchange membrane. The new filters are made of a very finely divided ion-exchange resin incorporated into a porous membrane structure of acrylic copolymer resin reinforced by light nylon fabric. Also available: a new 293-mm. disk filter holder designed to filter large volumes of liquids and gases. Gelman Instrument Co. **64**
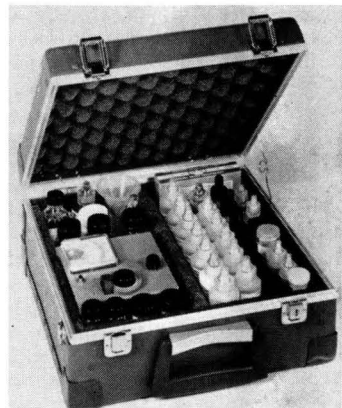
Waste Water Analysis Kit

Model 50 portable (11 pounds) laboratory is designed for water and wastes testing in public health, industrial, and agricultural applications. It is completely equipped for testing acidity, alkalinity, bromine, calcium hardness, carbon dioxide, chloride, chlorine, chromate, copper, total hardness, hydrogen sulfide, iron, manganese, nitrate, nitrite, pH, phosphate, sulfite, sulfate, and turbidity. Delta Scientific Corp. **65**

Charcoal for SO₂ Removal

Type CH charcoal, available in bulk or in air purification filters, was designed for enhanced capacity for adsorption of SO_2, according to the manufacturer. The product also has a high

Noise Measurement

The Mark IV noise exposimeter detects and records the total time a person is exposed to noise levels in excess of a preset limit—generally 80–100 decibels. Whenever noise levels exceed the preset threshold, the motor is activated and an indicator on the face of the device provides visual indication that the meter is recording. A counter indicates the length of exposure time in minutes. Union Industrial Equipment Corp. **62**

Miniature Pressure Transducer

Type 4-356 miniature pressure transducer is an unbonded strain gage instrument designed for test stand, high accuracy process control, and airborne applications. Pressure ranges from 0–10 to 0–500 p.s.i. absolute or gage throughout the temperature range $-320°$ to $+300°$ F. The unit provides 400-mv. full range output, with combined linearity and hysteresis rated by the manufacturer at ±0.25%. Bell & Howell Co. **63**

capacity for removal of other sulfur compounds such as SO_3, COS, and H_2S, other acid gases, and organic vapors, as well as most other contaminants found in both inside and outside air. Barnebey-Cheney Co.   **66**
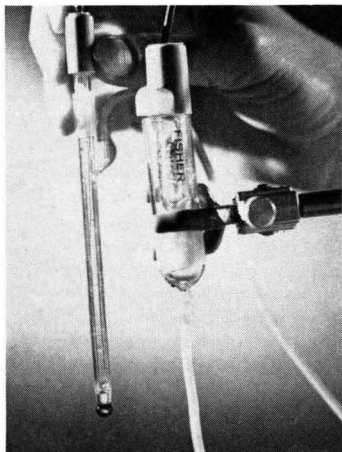
pH Meter

The Bio-Probe permits pH measurements of small biological samples without contamination of the sample by the electrolyte solution in the electrode. The device, which is 6 mm. in diameter by 5 inches long, requires only 0.2 to 3 ml. of sample for testing. Thus, the probe fits into centrifuge tubes and other small containers. Working pH levels range from 0 to 14, temperatures from $-5°$ to $+100°$ C. Fisher Scientific Co.   **67**

Dioxane Substitute

Bio-Solv solubilizers permit toluene to be substituted for the more troublesome and expensive dioxane, eliminating the handling problems and bad side effects associated with dioxane use, according to the manufacturer. The solubilizers are phase stable at both refrigerated and ambient temperatures, and provide high counting efficiency and repeatability. Beckman Instruments, Inc.   **68**

NEW LITERATURE DIGEST

Floating aerator for process water cooling

Model HS Floating Aqua-Lator is a self-contained lightweight aerator for converting existing holding ponds into process water cooling facilities. The submersible, propeller-driven pump draws water from a trough and sprays it into the air by high velocity pumping action. The spray falls into a catchbasin surrounding the narrow trough, and may be rechanneled into another trough for further cooling action.

All machined parts and castings of the unit are made from stainless steel or naval bronze and, according to the company, are virtually indestructible in normal use. In addition to cooling water and providing an attractive fountain for holding ponds, the unit is designed to strip gases such as CO_2 and H_2S. Welles Products Corp. **91**

Differential voltmeters. An 8-page brochure describing differential voltmeter products features a line of solid-state models for measuring e.m.f. to 1100 volts in four ranges with ±0.0025% accuracy. The illustrated booklet presents operating features and related operations of several models, including both a.c. and d.c. instruments. Honeywell, Inc. **92**

Recording pH meter. Bulletin 201 describes Model 30 analytical cordless recording pH meters for use in industrial and municipal water and waste water treatment facilities. The instrument can be line (a.c.) or battery operated, and includes a built-in recharger. The strip chart recorder for use with the unit does not require ink. Analytical Measurements, Inc. **93**

Fiber and water recovery. Bulletin Fiber 1 highlights machine modifications for modern pulp and paper mill operations. According to the company, the advantages of the process are elimination of conglomerate fiber mixing, elimination of sweetener additions in thickening, high capacity,

and flexibility of operation with low space requirements and low initial and operating costs. Dorr-Oliver, Inc. **94**

Slimicide. The merits of chlorine *vs.* acrolein as a slimicide for once-through and large recirculating cooling water systems are detailed in Technical Paper 209. Some case studies showing strong resistance to chlorine (mollusks and asiatic clams) but good response to acrolein are presented. Betz Laboratories, Inc. **95**

Miniplant laboratory equipment. A line of chemical process and laboratory equipment for small-scale operations (between test tube and full-scale operation) is presented in Bulletin 11. Included are bench-scale reactors, laboratory agitators and drives, continuous flow agitators, rotary and pneumatic dryers, high shear agitators, high viscosity mixers, a special paste mixer, and a laboratory deaerator. Bench Scale Equipment Co. **96**

Wet scrubbers. Catalog V-67 describes a line of high energy wet scrubber systems featuring abrasion-resist-

tant linings and automatic reamers. A variable venturi scrubber is also featured. Joy Manufacturing Co.   **97**

Water and waste treatment. A 12-page illustrated brochure, "Water and Waste Treatment Buyer's Guide," describes water and waste treatment equipment. For water treatment, the brochure considers aeration and degasification, clarification, filtration, softening, and ion exchange. For waste treatment, it discusses aeration, flotation, and ion exchange. Sanitary sewage systems include both package and custom designed plants, as well as various types of auxiliary equipment for sludge lines, sludge dewatering, and foam control. Ritter Pfaudler Corp.   **98**

Powders and particles. List No. 7 presents sized particles useful for preparation of aerosols, for standardization of particle-sizing instruments, and for surface area measurements. The list includes monosized particles, metallic and nonmetallic spheres, clear and colored plastic spheres, sized phosphors, and graded polens and spores. Particle Information Service.   **99**

Laboratory products. An 8-page bulletin (No. 5) describes a line of laboratory products, including a monochromator, micro-analyzer, cathodoluminescent device, 3000° F. gas lab furnace, crucibles, and other products. LeMont Scientific, Inc. **100**

Clarifier. Bulletin N-830 gives specifics on the Sediflcter clarifier for industrial and municipal waste treatment for waste water reclamation, material loss reduction, and waste disposal. Three pressurization systems offered in conjunction with the Sedifloter are described in a separate section of the bulletin. Other sections are devoted to design factors, treatment advantages, and suggested specifications. General American Transportation Corp.   **101**

ERB series recorders. Bulletin C-14 describes the ERB series electronic strip chart recorders, featuring photoelectric d.c.–a.c. converter and air purge connections for dirty atmospheres. As many as 12 variables can be recorded simultaneously (different colors) on the multipoint models. Foxboro Co.   **102**

PROFESSIONAL CONSULTING SERVICES

April 16–18
Air Force Cambridge Research Laboratories
5th Symposium on Remote Sensing of Environment
University of Michigan, Ann Arbor

The symposium will include presentations on sensors and vehicles, needs for remotely sensed data, data analysis programs and techniques, and problems limiting the use of remote sensing techniques. AFCRL cosponsors are the Office of Naval Research, Army Research Office, and U.S. Department of Agriculture.

April 16–18
University of North Carolina, and North Carolina State and Duke Universities
17th Southern Water Resources and Pollution Control Conference
Chapel Hill, N.C.

The conference will feature the technology of water resources and water quality management with particular reference to the southeastern U.S. Topics include the characterization of industrial wastes, tertiary treatment, instrumentation for determination of water quality, and a session on the problems of adoption and implementation of federal water quality standards by representatives of the southeastern states' water quality agencies.

April 16–19
Engineering Extension and the College of Engineering of the University of California (Berkeley)
Water Resources Engineering Educational Series (WREES)
University of California Extension Center, San Francisco, Calif.

Program V, "Economics and Public Policy in Water Resources Development," includes discussions of economics and public policy for agricultural water use, water pricing and water use, the role of public water districts, competing uses for water, economics of reservoir operation, planning and economics of recreational water use, input-output analysis of water use patterns, locations and factors influencing economic development, demand theory for water, and economics and public policy of ground water basins. Water developments and problems of California will be emphasized.

April 19–20
Extension Division and Environmental Health Research Center of the University of Missouri
Environmental Engineering Conference
University of Missouri, Rolla, Mo.

The areas of water resources, water pollution, air pollution, solid wastes, urban affairs, and environmental health planning will be discussed at this conference, whose theme is "Man, Engineering, Environment." Write: Dr. S. G. Grigoropoulos, Environmental Health Research Center, University of Missouri, Rolla, Mo. 65401

MEETING GUIDE

April 26
Air Pollution Control Association—Mid-Atlantic States Section
1968 Spring Conference
Hotel Dupont, Wilmington, Del.

The theme of the semiannual technical conference is "The Legal Road to Cleaner Air." The morning session includes papers on Delaware and federal air pollution legislation and the legal aspects of air pollution control from the state level. The afternoon session features papers on compacts and legislative intent.

April 28–May 1
Institute of Environmental Sciences
14th Annual Technical Meeting and Equipment Exposition
Chase-Park Plaza Hotel, St. Louis, Mo.

The theme of the meeting centers on new horizons and places emphasis on the application of environmental technology to the fulfillment of man's desire for a healthier, happier, and more peaceful life. Topics include space, earth, and marine environments; human factors; management; and others.

April 29–30
American Medical Association
5th Congress on Environmental Health Problems
Drake Hotel, Chicago, Ill.

The congress will focus attention on the goals and recommendations of the special report, "A Strategy for a Livable Environment." Commonly called the "Linton Report," this report to Secretary Gardner of HEW offers suggestions for solving environmental problems. The purpose of the congress will be to review and evaluate recommendations contained in the report and to examine the role of the medical profession in implementing some of the goals.

May 5–8
Incinerator Committee of ASME
3rd National Incinerator Conference
New York Hilton Hotel, New York City, N.Y.

Sessions are planned on air and water pollution control, refuse and residue qualities and characteristics, incinerator planning, incinerator design, and industrial incineration. Write: Mr. Leo Cohan, program chairman, 1968 National Incinerator Conference, % Combustion Engineering, Inc., Windsor, Conn. 06095

May 30–31
Vanderbilt University
7th Annual Sanitary and Water Resources Engineering Conference
 Noel Hotel, Nashville, Tenn.
Sponsored by Vanderbilt University School of Engineering, the State Department of Public Health, and the State Water Pollution Control Board, this conference is devoted to the design and operation of treatment processes for municipal and industrial wastes, hydraulic and hydrologic aspects of waste water collection, and disposal systems. A 1-day session on atmospheric pollution and control will be held concurrently.

June 6–7
Texas Water Pollution Control Association
8th Industrial Water and Waste Water Conference
 Koko Inn, Lubbock, Tex.
The theme of the conference will be water reuse management and measurement in industry. Conference topics will include industrial water systems, waste water treatment, pollution control, and problems of feed lot operations.

June 10–14
Gordon Research Conference on Environmental Sciences and Engineering
Surface Phenomena in Aqueous Systems
 New Hampton School, New Hampton, N.H.
Discussions are planned for sorption at the solid-water interface, coagulation and flocculation, filtration, and membrane processes. On the final day, presentations originating from the conference will be scheduled. As usual at Gordon Research Conferences, discussions are informal, and attendance is limited. For a complete schedule of the symposiums, see ES&T, January, page 74. For further registration information, contact Dr. W. George Parks, director, Gordon Research Conferences, University of Rhode Island, Kingston, R.I. 02881.

June 10–14
Manhattan College, Federal Water Pollution Control Administration
Thirteenth Summer Institute in Water Pollution Control
 Manhattan College, New York (Bronx), N.Y.
Advanced study courses will be offered in stream and estuarine analysis and in biological waste treatment. Fee for each course is $150, but stipends and travel allowances are available for qualifying U.S. citizens. Write: Dr. Donald J. O'Connor, Civil Engineering Dept., Manhattan College, Bronx, N.Y. 10471.

INDEX TO ADVERTISERS IN THIS ISSUE

Circle No. 19 on Reader's Service Card ⟶

CLIMET INTRODUCES A DIGITAL DATA
COLLECTION SYSTEM
YOU CAN AFFORD
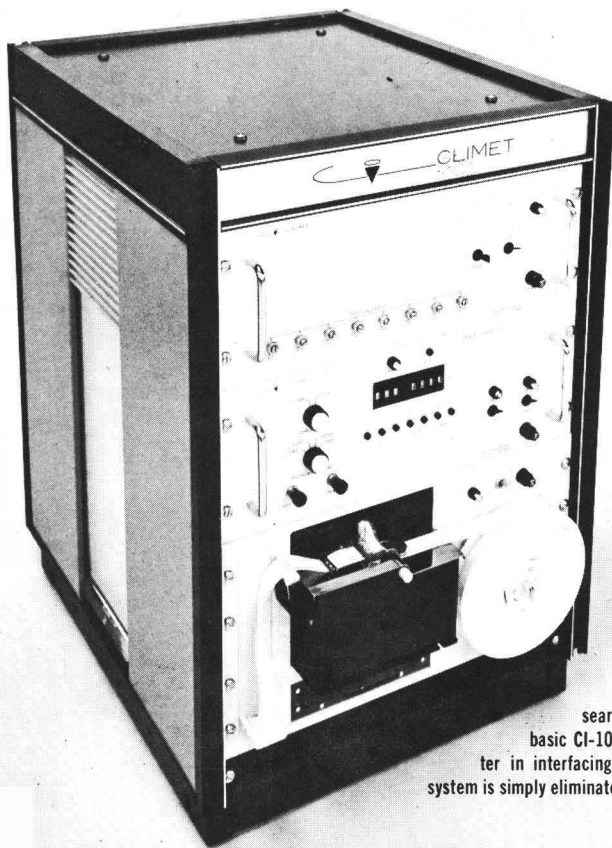
ECONOMY

With the new CI-100 Programmed Digital Data Collection System, **CLIMET** has dramatically reduced the cost of adding digital data handling to your present environmental monitoring system.

CI-100

The CI-100 automatically samples up to 20 environmental sensors and records their output data in digital form on either punched paper tape or computer-compatible magnetic tape. Because we've designed the CI-100 for volume production as a standard product, we can offer this equipment for half the cost of a typical "one-of-a-kind" data collection system of similar capabilities.

VERSATILITY

To allow us to schedule volume production of a single all-purpose digital data handler, we designed the CI-100 as a versatile system capable of time-programmed sampling, digital encoding, and recording nearly all the analog signals generated by environmental sensors commonly used in air pollution research projects. As this versatility is pre-engineered into the basic CI-100 system, much of the cost and delay you might encounter in interfacing your existing sensors to a new digital data collection system is simply eliminated.

DETAILS

Write or phone for a comprehensive brochure on the **CLIMET** CI-100 Programmed Digital Data Collection System. We'll rush the brochure to you via return airmail, and include a free copy of Meteorological Instrumentation For Air Pollution Studies.

CLIMET
INSTRUMENTS INC.

1240 BIRCHWOOD DRIVE, SUNNYVALE, CALIFORNIA 94086   TELEPHONE (408) 736-6950

fume clean-up

In metal decorating, printing, or other coatings circles, UOP is well known for its catalytic incinerator systems which oxidize waste solvent vapors in oven exhaust air . . . with excellent economy. □ As the pacesetter in the art of air correction, UOP offers systems and equipment to best control your solvent emissions. Thermal incineration, as in the installation shown above, can be a better choice, under certain conditions. □ And at UOP, you get the choice. UOP's engineering group will specify the most efficient and economical system for your individual needs. UOP Air Correction Division, Universal Oil Products Company, Greenwich, Connecticut 06830.

better ideas from **LOP**

Petroleum & Petrochemical Processes · Transportation Equipment · Plant Construction · Chemicals & Plastics · Fragrances · Air & Water Management

Circle No. 30 on Readers' Service Card