

ENVIRONMENTAL Science & Technology

Emphasizing

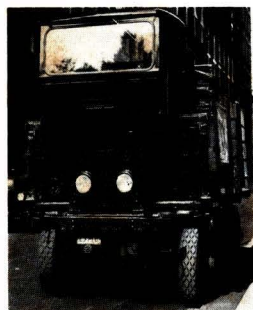
Water,

Air, &

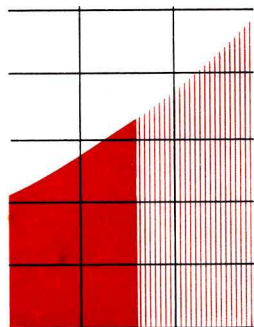
Waste

Chemistry

MARCH 1967

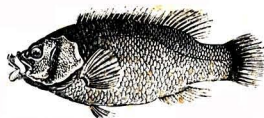


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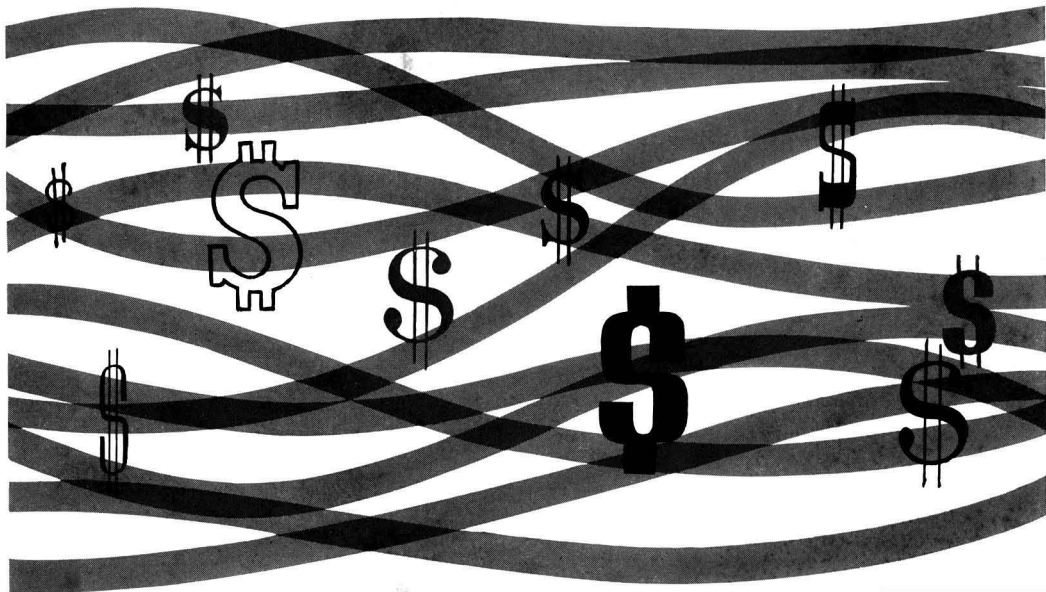
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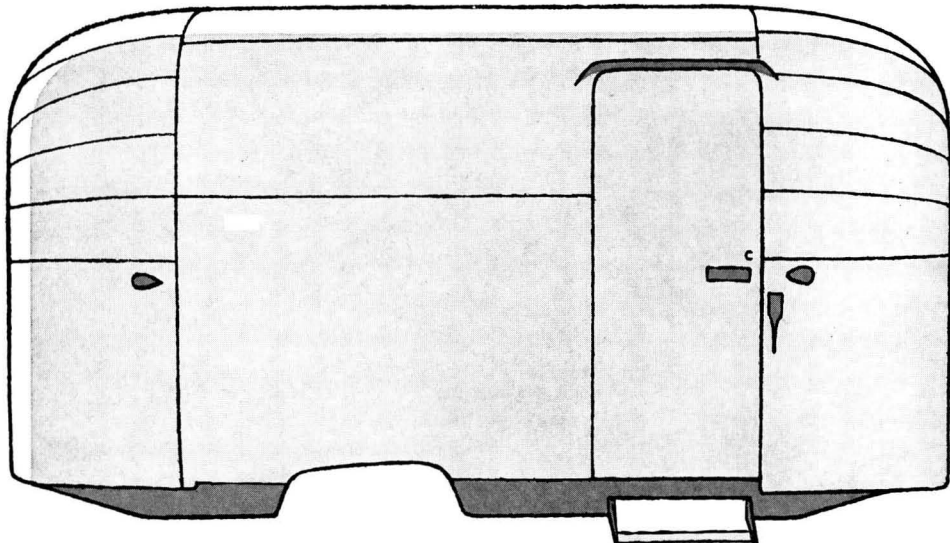
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Werner Stumm, Heinz Hüper, and Robert L. Champlin 221

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The surface chemistry of active carbon: A discussion of structure and surface functional groups

Vernon L. Snoeyink and Walter J. Weber, Jr. 228

Active carbon is an effective adsorbent for removal of dissolved organic substances from waters and wastewaters. The physico-chemical nature of the surface of carbon is an important factor in the adsorption process and should be considered in selection or preparation of carbons for specific uses. Active carbon is a complex adsorbent, the properties of which are dependent upon the raw material from which the carbon is prepared, the temperature of activation, and the types of oxidants and other additives employed in the activation process. These variables all affect the formation of the microcrystallite, the basic structural unit of active carbon. It is these same variables that affect the chemical nature of the microcrystallite surfaces and, thus, the sorptive properties of the carbon and its interactions with solutes in solution.

Ion exchange processes for the reclamation of acid mine drainage waters

Frank Pollio and Robert Kunin 235

Acid mine drainage water is a serious water pollution problem in many parts of the U.S. as well as throughout the world. In Pennsylvania alone nearly 1.4 billion gallons of acid mine waters are discharged daily. One solution to the problem is to prevent such drainage water from reaching the streams, a rather difficult task. Another is to treat the water and reclaim it for industrial, agricultural, or domestic uses. Using a treatment system based on the conventional gel anion exchange resin, Amberlite IRA-68, the authors have managed to process water at costs of between 25 and 50 cents per 1000 gallons, although the cost depends on regenerant costs, feed water quality, and desired end product water quality.

Evaluation of various silica gels in the gas chromatographic analysis of light hydrocarbons

T. A. Bellar and J. E. Sigsby, Jr. 242

Gas chromatography is an important tool in air pollution studies and research for the analysis of complex hydrocarbon mixtures. The authors had previously described a detector and column system which could be used for precise, quantitative analysis of most hydrocarbons while avoiding interferences caused by other compounds. However, the silica gel packing material for the column is no longer available. So the authors have suggested alternatives. Commercially available silica gels with an average pore diameter of around 150 Å can be used for the analysis of C₁ to C₆ paraffins, C₂ to C₂ olefins, and acetylene. By modifying the 150 Å silica gel with trace quantities of water or common polar liquid phases the chromatogram can be extended to include all the C₄ olefins with 100% resolution between butene-1 and isobutylene.

Analysis of the oxidant in photooxidation reactions

I. R. Cohen, T. C. Purcell, and A. P. Altshuller 247

Because of their deleterious effects on plants and animals, oxidants are routinely measured and reported as one of the components in photochemical-type air pollution. However, the usual procedure involves the manual or instrumental measurement of these materials with solutions containing potassium iodide, which reacts with oxidants at widely varying rates. Thus, the usual quantitative figures for the presence of oxidants may be misleading. To obtain more meaningful data, the authors propose ferrous thiocyanate reagent for total oxidant, neutral and catalyzed potassium iodide solutions for differentiating between "slow" and "fast" oxidants, and, under controlled conditions, a titanium reagent specific for hydrogen peroxide.

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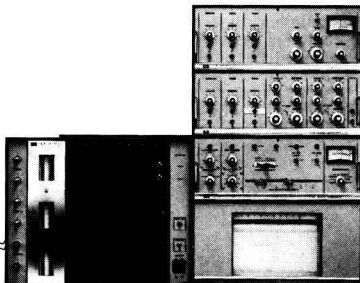
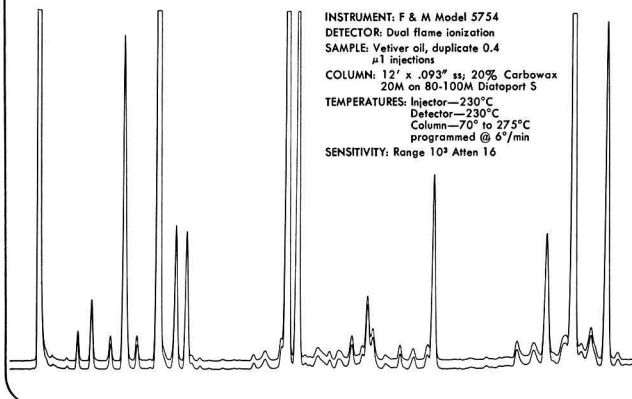
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Ground-Water Resources

In what the U. S. Geological Survey describes as the first comprehensive description of the nation's single most productive ground water source, V. T. Stringfield of the USGS's Water Resources Division, notes that orderly, scientific withdrawal of water is needed to preserve the Floridian aquifer, the water-bearing limestone formation underlying 90,000 square miles of portions of South Carolina, Georgia, Florida, and Alabama. The potential problems, says Mr. Stringfield, are local depletion, contamination from encroachment of salt water, and indiscriminate disposal of waste waters. The aquifer now supplies more than 2 billion gallons of water daily; and it will be penetrated by hundreds of thousands of additional wells in the next 10 to 20 years. The Floridian aquifer, as this fresh-water portion of the U. S. ground water source is known, might even be suitable for carefully controlled disposal of wastes in a saline water zone at depths ranging from 2000 to 3500 feet. USGS is also constructing an electrical analog model of the aquifer to provide a scientific basis for future control measures.

In more immediate danger are the ground-water resources of eastern North Carolina, in areas of large-scale phosphate mining. Artesian pressures throughout the area are dropping because of intense pumping at the mine sites. This removal of water from the ground supply has caused natural percolation to reverse, so that in some places—especially in the estuary of the Pamlico River upstream from the pit—brackish water from the river will move into and contaminate the ground-water, says a consultant's report to the North Carolina Board of Water Resources.

Industrial Antipollution Program Support

The League of Women Voters has issued a statement strongly supporting federal financial aid to speed private industry's pollution abatement programs. Though convinced that the costs of cleaning up polluted rivers and streams are essentially the responsibility of the polluters, the league feels that the "urgency of this special situation and the enormous sums of money involved" require not only strict enforcement of antipollution laws, but also limited allocation of federal funds on the basis of critical local needs. Forms suggested for such aid include long-term, low-interest loans and federal grants to support industrial research on new methods for halting pollution. National League president, Mrs. Robert J. Stuart, who issued the statement following consideration by the board of directors of hundreds of reports submitted by local league groups, said that proposals for state financial aid to industry are expected to be introduced in many state legislatures this year. Meanwhile, an official Government report on the costs and forms of potential federal aid is being prepared, the result of a joint study by the Departments of Treasury and Interior under a provision of the 1966 Clean Waters Restoration Act. (For further details of the League of Women Voters' long history of interest and action in the field of water pollution see page 261.)

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Cleaner Air Week Awards

The Air Pollution Control Association has granted certificates of award for outstanding educational activities conducted during Cleaner Air Week in the fall of 1966. APCA's awards, which went to 30 U. S. cities, metropolitan areas, state and county health departments, and three areas of Canada, included Blue Ribbon Awards for special achievement to Birmingham, Ala.; Boston; Connecticut State Department of Health, Hartford; Laurel and Billings, Mont.; Muskegon, Mich.; New York City; Providence, R. I.; Texas State Department of Health, Austin; and metropolitan Toronto. More than 90 communities, metropolitan areas, and states participated in the 1966 program.

Water Resources Planning Grants

The Water Resources Council has granted \$585,230 to 32 states in initial planning grants under the Water Resources Planning Act of 1965. Purpose of the grants is to encourage increased comprehensive planning by the states in development of water and related land resources. This is the second allocation of planning funds and makes a total of \$704,190 awarded to 38 states. For fiscal 1967, 46 states have applied for portions of the \$1.7 million appropriated, the funds being allocated on the basis of population, land area, per capita income, and the distribution of allotments.

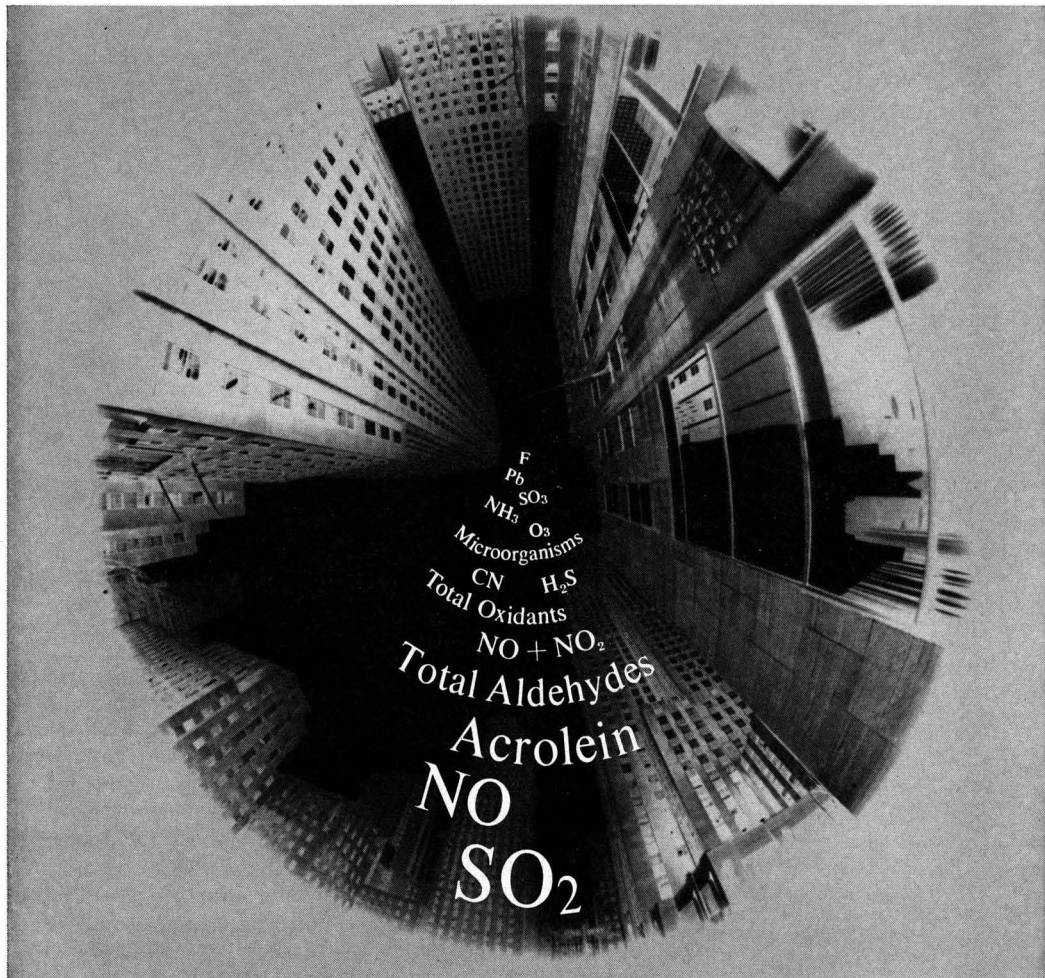
Interstate Air Pollution

A recommendation for a strong interstate agency to control air pollution in the New York City-Northern New Jersey metropolitan area came from a conference sponsored by HEW earlier this year. Agency members would include the Federal Government, New York State, and New Jersey, each of whom would have equal votes. Also included in the list of recommendations generated during the two-week conference were proposals to speed up the use of low-sulfur fuels in existing power plants—fuels could contain no more than 1% sulfur after October 1, 1969. By that same date, high-sulfur fuels for heating and for uses other than power plants would have to be halted. Further, after July 1 of this year no new power generating facilities or expansion of existing facilities would be allowed in the metropolitan area unless there were an assured 20-year supply of low sulfur fuel.

The conference participants also recommended that sulfur dioxide emissions be limited to 2000 p.p.m. at existing plants and 500 p.p.m. from new sources. And, finally, they recommended that because the Federal Government and both states require exhaust controls on all new automobiles (starting in 1968) the states monitor atmospheric levels of carbon monoxide and advise the Secretary of HEW of any apparent need for more stringent new motor vehicle control standards. Meanwhile, each state was admonished to encourage industries within their jurisdiction to control carbon monoxide levels.

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Water Pollution R&D Grants

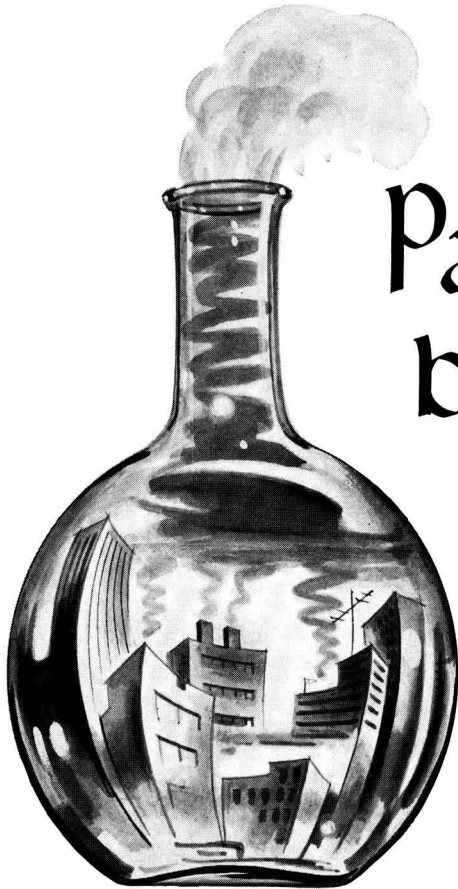
Contracts and grants totaling approximately \$20 million were awarded in 1966 by the Federal Water Pollution Control Administration. Included among these, according to Secretary of the Interior Stewart L. Udall, were the first ever made by the FWPCA to private industry and industrial organizations. About half the total was spent in search of improved methods for dealing with overflows from combined sewers, a problem of serious consequence in a number of America's largest cities. Thousands of miles of these sewers, built before the danger of river and lake pollution was fully recognized, are incapable of carrying both sewage and storm water following heavy rains or snows with the result that diluted, untreated sewage escapes. Cost of replacing combined sewers by separate sewers—a partial solution since storm water runoff remains—could reach \$20 to \$30 billion.

Seeking a less costly alternative, Congress has authorized grants to cities attempting other solutions. Nine cities were awarded a total of slightly more than \$8 million in 1966 to help finance such projects as construction of large detention basins to hold combined sewer overflow prior to treatment and installation of automated sewer regulator stations designed to provide better control of combined flows. In addition, contracts totaling \$1.6 million were let to 10 private companies to examine such possibilities as building a sewer within a sewer or constructing submerged containers capable of holding combined sewer waste until it could be pumped back to water pollution control plants for treatment.

About \$10 million went to support R&D on industrial waste disposal and advanced waste treatment operations. Of this, 10 private companies and organizations received a total of \$2.6 million for waste disposal projects that have potential industry-wide application. Fourteen cities and local government districts were awarded grants totaling \$7.5 million for advanced waste treatment demonstration and research projects. In addition to the \$20 million spent on these new research programs, FWPCA spent close to \$18 million in 1966 on its basic general research program, the goals of which include reducing water pollution from mine acids, preventing deterioration of water held in reservoirs, and purifying water for reuse.

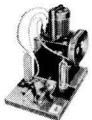
Rewards of Reforestation

Reforestation brings cash returns, as well as conservation benefits, says a recent TVA study. In the 1940's, TVA reforested the 88-acre Pine Tree Branch watershed in Tennessee, where erosion had been carrying away an average of 24 tons of soil per acre annually. Rapid water runoff after storms was contributing to local flooding. (This small watershed is typical of thousands of acres of idle lands in north Mississippi, west Tennessee, and west Kentucky.) Within 15 years after reforestation, annual soil loss had dropped to 4% of the 1940 level, and storm water was reaching the stream more gradually. Now, timber harvesting has begun. TVA foresees a total return of \$60,000 at the end of 45 years, when all the timber has been harvested.



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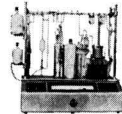
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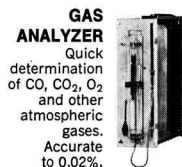
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Desalination Plants and Grants

Plans are proceeding for a nuclear-fueled combination power-desalination plant in Orange County, California. The plant would produce 150 million gallons of distilled water a day (enough for 75,000 people) and 1800 megawatts of electric power (more than that produced by Hoover Dam). The Metropolitan Water District of Southern California, which will operate the plant, is putting up \$126 million of the total capital costs of \$444 million; \$257 million will come from utility companies, \$61 million from the Government (plus \$11 million in federal money for operating costs). Power costs at the dual-purpose plant will be no greater than at a single purpose nuclear power plant of the same size at the same location. Water costs from the multistage flash evaporation units will probably be about 20 cents per 1000 gallons. The cost of Colorado River water now supplied by the district is less than 10 cents per 1000 gallons. Construction will be in stages, the first portion slated for operation in 1972, the last in 1977.

The Virgin Islands Water and Power Authority dual purpose plant will be operating much earlier—by mid-1968. Baldwin-Lima-Hamilton Corp. will build the \$6.3 million plant, which will be capable of producing 2.5 million gallons of water per day (multistage flash evaporator) and 15.5 megawatts of power. The plant will triple St. Thomas Island's fresh water resources.

Emphasizing the continuing interest in saline water conversion are the 44 contract awards totaling \$3.1 million made in this subject area by the Office of Saline Water. All told, OSW awarded 60 such contracts totalling \$3.7 million in the last six months of last year.

Eddies

Washington, D.C., physician prescribes small charcoal-filled bags to be held to the nose and mouth of allergic persons making trips into the street-fume laden areas of downtown. . . Miami Beach's high clean air rating in a joint federal-state report on Florida air is denied by P. W. Leach, director of Dade County (Miami) Health Department's Air Pollution Bureau. . . Dr. R. A. Bryson, University of Wisconsin meteorologist, says that atmospheric dustiness may be responsible for the down-turn in the trend of world temperatures. . . Proponents of the "greenhouse effect" claim that the great quantities of carbon dioxide released to the atmosphere through the burning of fossil fuels is responsible for an increase in world temperatures. . . Citing evils of pollution from diesel buses, civic groups in Seattle, Wash., seek to save the remains of the city's trackless trolley system. . . Claiming that a lower demand for electricity from fossil fuel power plants will result in less air pollution, Pittsburgh, Pa., officials announce plans to replace trolleys with diesel buses. . . AFL-CIO Executive Council urges state and local groups to push for strong state and local air and water pollution control programs. . . The National Academy of Sciences and the National Academy of Engineering have established an Environmental Studies Board to act as a national focus for broad interdisciplinary efforts to reduce or control pollution and other environmental problems.

OUTLOOK

ELECTRIC VEHICLES Revival of a 50-year old memory

*The car of choice at the turn of the century,
the electric car could well be the town-car of choice by 1980*

Pollution facts and forecasts

The PHS's Division of Air Pollution estimates that the daily emissions of the principal pollutants from motor vehicles for the entire nation amount to some 225,000 tons (based on 90 million motor vehicles), including 190,000 tons of carbon monoxide, 27,000 tons of hydrocarbons, and 9000 tons of oxides of nitrogen. These figures are based on estimates that 4.2 pounds of carbon monoxide, 0.55 pound of hydrocarbons, and 0.2 pound of nitrogen oxides are emitted per vehicle per day.

The American Automobile Association reports that in 1965 the number of passenger cars, including taxi cabs, was slightly more than 75 million and that these vehicles consumed 71 billion gallons of gasoline during that year. Correspondingly, the estimated tonnage of pollutants emitted by these vehicles was approximately 70 million tons.

The AAA estimates that by 1980 there will be 100 million passenger cars, including taxi cabs, and that they will use about 100 billion gallons of gasoline during that year. If vehicular pollution is not reduced, about 100 million tons of various pollutants will probably be emitted into the atmosphere by passenger cars during 1980.

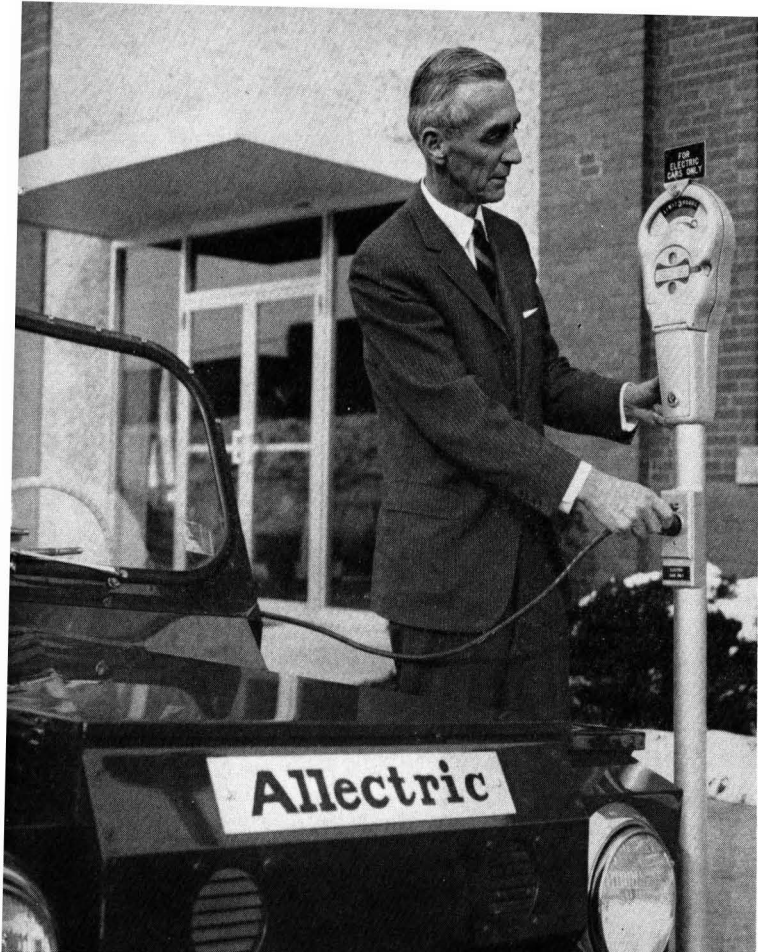
The electric powered vehicle is very much in the news today. What has led to interest in the comeback of the electric vehicle, which was common on American roads at the turn of the century?

One of the major incentives for the development of electric powered vehicles is the growing problem of air pollution. As the population of the U.S. expands, the per capita ownership of cars rises, and proportionately more people tend to live in cities than in rural areas. These factors serve only to complicate an already alarming pollution picture. Automotive exhaust fumes are the largest single contributor to air pollution, and the most annoying because the pollutants are injected into the air at ground level.

Urban air pollution by automobiles can be alleviated several ways: internal combustion engine redesign, more effective exhaust controls, different and novel methods of vehicular propulsion, electrified rapid mass-transit systems—and the development of effective electric vehicles.

Recent interest

Recently, various groups have expressed interest in the development of the electric vehicle. The Federal Power Commission has just issued a report on the development of electrically powered vehicles at the request of the Senate's Committee on Commerce. A National Electric Automobile Symposium was held in San Jose, Calif., February 24–25. In January the Technical Advisory Board of the Department of Commerce



Bright future. *Special electric lanes on interstate highways, automatic control of electric cars for long-range trips (perhaps while recharging the battery), third rails for electric power pick-up—these are only a few of the possible future developments for electric cars. In-town developments include parking meters that recharge batteries, such as this system by West Penn Power Co.*

tricity and higher efficiency of rectifiers, satisfactory operation for light delivery trucks and short-haul passenger car service could be obtained even with lead-acid or Edison-type batteries. Current electric energy costs of 1.4 to 2.0 cents per kilowatt-hour would result in energy costs of between 1.0 and 1.6 cents per mile for the electric car, which is less than the fuel cost for gasoline-engine driven vehicles, except for the very minimum weight types."

Another advantage of the electric car is ease of maintenance. The internal complexity of the internal combustion engine, particularly with the need to adjust engines for minimum emissions, requires an ever-increasing amount of attention. The electric car requires only occasional filling of the batteries and lubricating of chasis grease fittings. A major overhaul amounts only to dressing the commutator and replacing brushes.

Mr. John A. Kirtland of FMC Corp. makes the point that the only moving parts of the electric engine are the reduction gears and rotors of the alternator and motor. Electric braking reduces mechanical brake maintenance. Automatic system controls prevent self-damaging effects to power-train components and extend engine life. In addition, the modularization of the various drive components allows quick and easy removal and replacement when any repair is required.

The electric car is versatile. With drive-train components connected by cables instead of drive shafts, drive

established a panel on electrically powered vehicles to undertake a thorough study and then to report to the board between October and December. And on April 6, 7, and 8 a symposium, Power Systems for Electric Vehicles, is scheduled at Columbia University.

The electric vehicle can barely begin to compare with the combustion-engine-driven vehicle for long-range, high-speed travel. But the fact is that 91.8% of all trips are for distances shorter than 20 miles, and these account for 48% of all mileage.

Stop-and-go driving, with its frequent periods of deceleration and idling, is a very inefficient way of using gasoline. Moreover, since release of hydrocarbons is 10 times greater during deceleration than during acceleration, release of pollutants into the air is greatest during stop-and-go driving common to city travel.

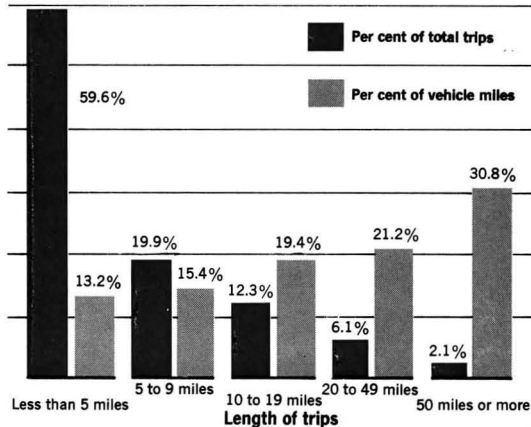
The electric vehicle could easily serve as a short-distance, in-town, stop-and-go vehicle for these short trips which make up the bulk of American travel.

Advantages of the electric car

Electric cars are quiet, odorless, and probably will be considerably more compact than standard cars. Electric cars do not use energy when the car is stopped (except for accessories). The electric motor has speed and torque characteristics far superior to the combustion engine for stop-and-go driving.

Dr. Howard A. Wilcox of General Motors cites as potential advantages of electric cars, "quiet operation, efficiency not limited by heat engine cycle, freedom from emissions, and use of low-cost electricity generated by nuclear reactors when fossil fuels become more scarce." Mr. Bradley Cozzens of the Los Angeles, Calif. Department of Water and Power adds, "The car does not require the idling of the motor when it is parked for delivery purposes, immediately starts upon getting in and operating the controller, and is a particularly quiet device for travel in city streets, such as for milk trucks on early morning deliveries. Second, with the current rates for elec-

More than 90% of car trips are for distances less than 20 miles



points and power sources can be located at a variety of points in the vehicle, allowing multiple-wheel drives, trailers with power-driven wheels, and the like. This flexibility provides smooth, absolute, and precise control of the tractive effort at all drive points, thereby preventing slipping or running away of one wheel with respect to any other.

Finally, and no small advantage, the electric car is able to start in all types of weather, and has quick pick-up.

Capabilities of the existing prototypes

Naturally, electric power companies are encouraging research in electric cars; and car manufacturers are trying to capture the potential market. General Motors used a 530-volt silver-zinc battery in its 1966 experimental car, Electrovair II, and demonstrated a range of about 75 miles, top speeds of 80 m.p.h., and an acceleration rate of 0 to 60 m.p.h. in 16 seconds. Operation of the car compares favorably with the Corvair, a gasoline-driven GM car.

West Penn Power designed and built a new solid state speed control system for its \$2000 electric car, capable of speeds of 50 m.p.h. and 50 miles between charges.

Yardney Electric has been testing a modified Renault Dauphin using four aviation-type Silvercel batteries about the size of conventional batteries and weighing a total of 240 pounds. The car reaches a top speed of 55 m.p.h., has a range of 77 miles, and accelerates from 0 to 30 m.p.h. in 5 seconds.

A dyna-Panhard model car, converted for electric operation in France in 1954 (using a specially-designed silver-zinc battery), achieved speeds of 50 m.p.h., a range of approximately 120 miles on one charge of the battery, and an acceleration rate equal to that of a gasoline engine car.

Sintered alkali batteries, hydrogen-oxygen fuel cells, and other, exotic power sources have been tested as methods of electric vehicle propulsion, some with promising initial results, but extensive research is needed on all types of cells before mass production of any one is contemplated.

Disadvantages of electric cars

If an electric car were placed on the market today, it would cost more than the gas-propelled cars available now, and would offer poorer performance (considering range between refuelings,



Vintage truck. Still in use in Philadelphia after 50 years of service, this Curtis Publishing Co. electric truck costs about 25 cents per day to operate

Characteristics of automobile exhaust gas change with type of driving

Exhaust	Idle	Deceleration	Cruise	Acceleration
Flow (standard cubic feet per minute)	6	6	35	60
Muffler temperature (°F.)	500	500	700	900
Composition (volume %)				
Nitrogen	70.4	70.4	73.2	71.0
Water	13.0	13.0	13.1	13.2
Carbon dioxide	9.5	9.5	12.5	10.2
Carbon monoxide	5.2	5.2	0.8	4.2
Hydrogen	1.7	1.7	0.2	1.2
Total	99.8	99.8	99.8	99.8
Hydrocarbons (p.p.m.)	750	4000	300	400
Nitrogen oxides (p.p.m.)	30	60	1500	3000

Weight problem. *The major drawback of available battery systems is their size and weight. In GM's Electrovair II, the 1230-pound power train fills the front end, the trunk, and part of the space under the rear seat*



rechargings, cruising speed, acceleration, and convenience in operation).

Although the electric car would not itself be polluting the air, it would draw power from a central power-generating plant that burns a fuel—probably coal or fuel oil. This plant would contribute sulfur oxides, nitrogen oxides, and carbon pollutants to the air.

Even nuclear reactors have their own pollution problems, since radioactive waste products are generated. The fact is, however, that almost any power system, considered in toto, presents some sort of pollution problem.

Prototype cars shown so far have been powered in most cases by extremely expensive silver-zinc cells where performance was acceptable. The major stumbling block to the early mass use of an all-electric car is the present lack of a sufficiently high-power, high-energy-capacity storage or fuel battery at reasonable cost.

The practical possibilities for vehicle propulsion are reduced to these:

- Fuel cells operating on a storable fuel and using air as a cathode depolarizer (oxidizer).
- Electrically regenerative fuel cells; that is, devices fundamentally analogous to a storage battery.

	Electrovair II	Corvair
<i>Weight</i>	3400 lbs.	2600 lbs.
<i>Performance 0-60 m.p.h.</i>	16 sec.	16 sec.
<i>Top speed</i>	80 m.p.h.	86 m.p.h.
<i>Range</i>	40-80 miles	250-300 miles
<i>Power train weight</i>	1230 lbs.	610 lbs.

- Metal-air hybrid cells.
- Rechargeable battery systems—aqueous type (ambient temperatures).
- Rechargeable battery systems—fused salt type (ambient temperature).
- High energy battery systems—non-aqueous type (ambient temperature).

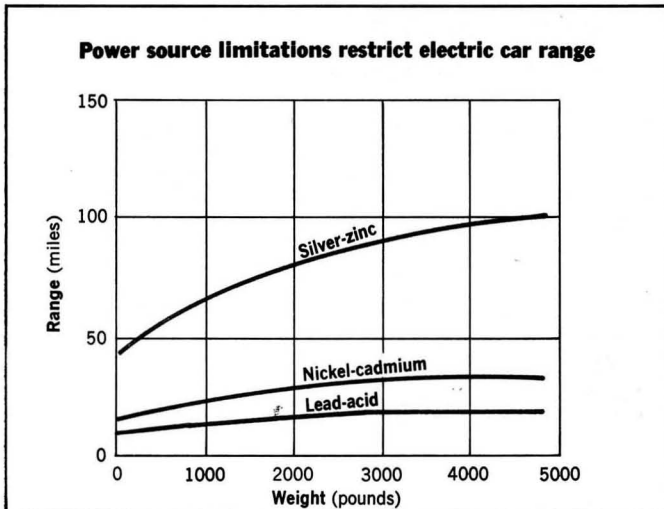
Fuel cell—storable fuel systems

There are today no difficulties in equipping a vehicle with **hydrogen-oxygen fuel cells**, provided the size of the vehicle is not a factor. The weight of the tankage, however, is a serious problem for small, passenger-car type vehicles. The alternative, very low temperature storage, is prohibitively expensive and calls for boil-off of hydrogen even when fuel is not used. Furthermore, hydrogen fueling presents a formidable safety problem.

The greatest hope for vehicle propulsion in this category appears to be in the hydrocarbons. However, these cells require large amounts of precious metal catalysts, which are unstable (they tend to poison the systems) and too scarce for mass use.

Gaseous, rather than solid materials, are the products of **electrically regenerative fuel cells**, which seem to have little to offer as a power system for a vehicle. It would require a heavy, separate loop for handling oxygen in a closed system. Polarization (with its consequent energy penalties) is a constant problem with electrically regenerative systems.

Among metal-air hybrid systems, the



alkaline zinc-oxygen or air system so far appears the most promising. Rechargeable types, however, have a short cycle life due to dendritic electrocrystallization of the zinc upon recharging. There is considerable weight penalty involved because of the need for air cathodes. Rechargeable forms of the metal-air hybrids probably cannot provide energy densities in excess of 80 watt-hours per pound.

The most well-known of the aqueous battery group is the silver-zinc. This battery cannot be sealed because a small, spontaneous generation of hydrogen gas occurs on open circuit stand. All designs for vehicles with such batteries point to a distance range of only 40 to 60 miles. The one most serious objection to the silver-zinc battery, however, is its cost. Individually priced in excess

of \$12,000, even mass production cannot bring the initial investment in this battery within the range of most potential electric car buyers.

Fused-salt battery systems will probably never offer a start-up time less than 30 minutes, which is totally unacceptable to the average consumer. Corrosion problems handicap all molten salt systems. In addition, some of the fused-salt systems (sodium-sulfur, for instance) are potentially violently explosive.

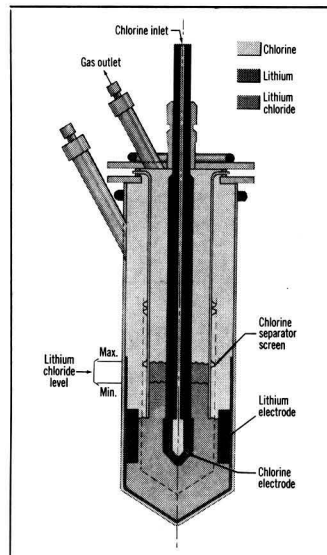
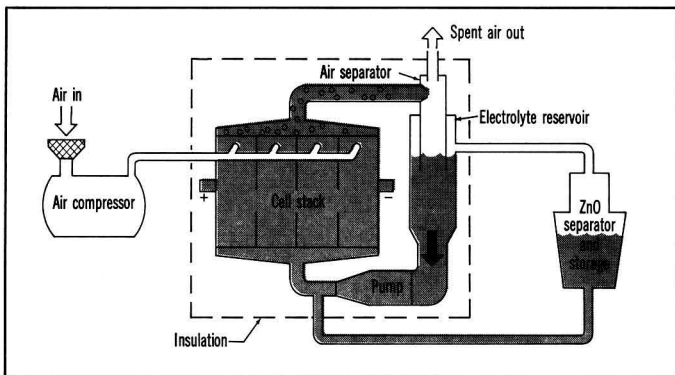
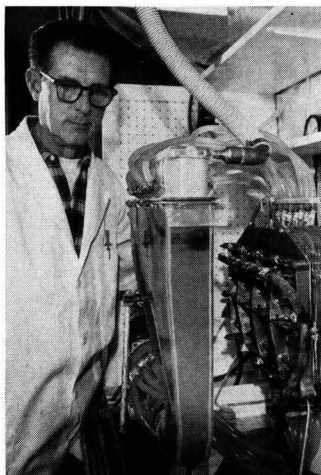
Nonaqueous batteries based on lithium offer substantially larger theoretical energy densities than the usual aqueous battery. Reasonably successful results have been obtained from secondary batteries of lithium-silver chloride; lithium-copper chloride; and lithium-nickel fluoride. The rechargeability characteristics of these batteries have

not been fully ascertained yet; these are relatively new concepts, still in the laboratory stage. When mass-produced, the lithium battery will probably not be costly.

Acceptable top speeds and distance ranges for an electric automobile require energy density characteristics of 140 watt-hours per pound or more. With the exception of the possible future development of a practical and economical hydrocarbon fuel cell, the lithium battery operating on organic electrolytes in the vicinity of room temperature appears to offer the only reasonable hope for meeting this basic requirement. In the final analysis, the energy-density factor must, and will, be the deciding factor in the eventual choice of the power source for an electric vehicle.

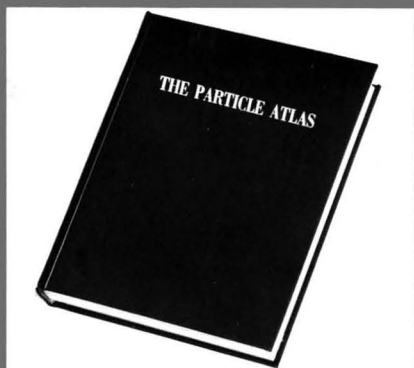
R&D continues as industry seeks the perfect battery

Zinc-air. *Despite high weight requirements and a tendency to form dendrites, hybrid cells probably deserve further investigation. The alkaline zinc-air system manufactures energy from the photochemical process of converting zinc to zinc oxide (schematic, below; prototype, right). Zinc is stored in the form of metallic zinc plated on inert backing sheets. Air, pumped through porous nickel electrodes, provides the necessary oxygen. Aqueous potassium hydroxide is circulated through the stack. The product, zinc oxide, is swept away by the electrolyte and carried to a zinc oxide separator where it is stored in a relatively dry state.*



Lithium-chloride. *Nonaqueous organic electrolyte batteries, such as this recently unveiled GMC cell, seem promising*

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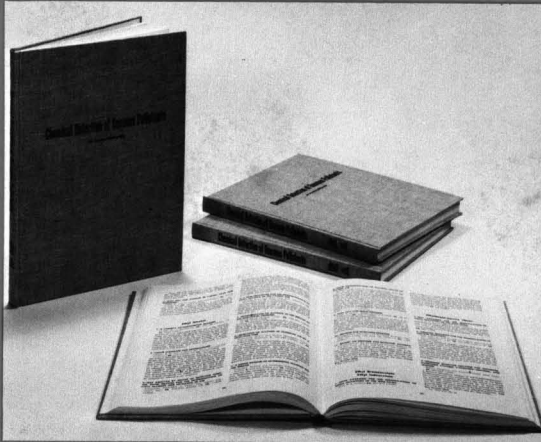
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Solid Wastes

Garbage, trash, scrap, waste. Call it what you will. Burn it, bury it. Reuse it somehow. Get rid of it. No matter what you do with it, you can't forget it—and meanwhile it's costing you \$2 to \$3 billion annually

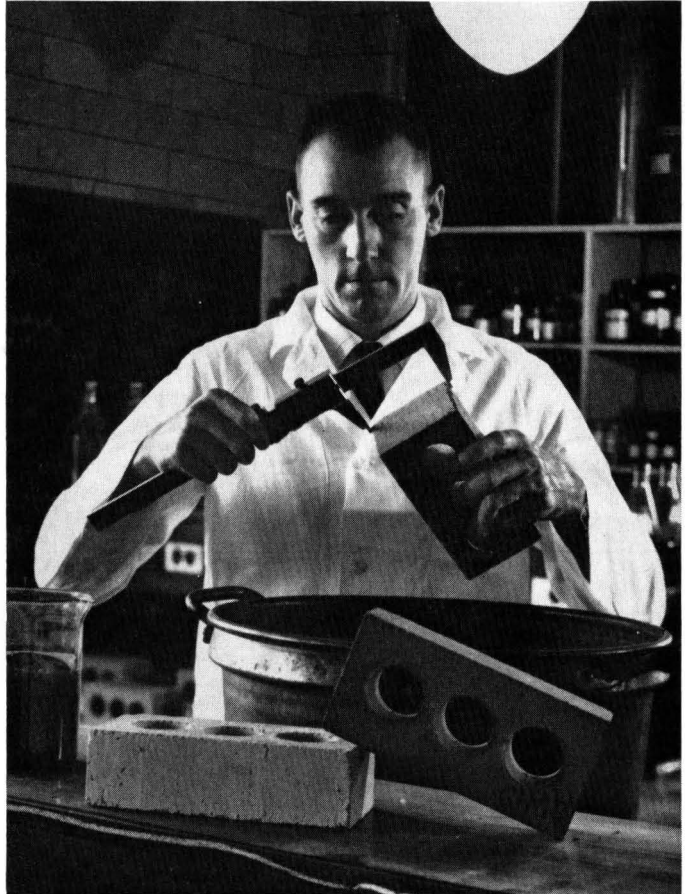
Each year U.S. citizens must collect and dispose, in some fashion or other, some 250 billion pounds of solid waste per year—a little bit less than 1500 pounds per capita per year, a little bit less than 4 pounds per capita per day. And that doesn't account for all the solid waste that is disposed of each year.

Try to categorize it and the mind boggles. Look at it and list it and the head reels. Almost a billion pounds of solid waste per day—and hardly anyone cared, until lately. The mountain of daily discards is steadily advancing on the civilization that is creating it, threatening to destroy the soil, foul the air, and dirty the water.

Solid waste became a real problem because of many years of public apathy. Most Americans neither knew nor cared what happened once their garbage was picked up or dumped in the garbage disposer. The federal and local governments shared in this apathy.

Old cars just die, they don't fade away. The slag heaps get bigger as if intent on destroying the countryside through their very bulk or the acid waters from them. Disposal of agricultural products becomes more of a problem as production rises to meet the demands of a growing population. The paper pollution problem, the cans, the bottles, the plastic containers—and on and on in a bewildering array and at a fantastic pace. If the world is going mad it seems destined to do so surrounded by the artifacts of its civilization.

But there are some signs of change. Under the authority of the Solid Waste Disposal Act of 1965 (ES&T, January,



Fly Ash. *More than 20 million tons of fly ash accumulate each year at domestic power plants. Currently the U.S. uses only 4% of this material. But new uses, such as making brick that contains 97% coal ash and fly ash, offer an effective disposal means and a useful and inexpensive end product for construction*

page 18), the U.S. is forging a national program of research, demonstrations, training, and planning, in the field of solid waste disposal. The expenditures authorized for the fiscal year 1967 total \$20 million (\$14 million to HEW, \$6 million to Interior). Now, a year and a half after the act was passed, these funds are being disbursed in the form of grants and contracts. Prior to the passage of the act, the Government's annual expenditure for solid wastes research was about \$250,000.

More evidence of continuing interest in solid waste disposal: A test-demonstration project is under way in Maryland where abandoned strip mines will be used for the disposal of solid wastes (ES&T, January, page 11). And a co-operative team of experts from Consolidated Edison (N. Y.) and New York City's departments of sanitation and air pollution control is touring refuse incineration-power generating facilities in Munich, Stuttgart, Dusseldorf, Paris, Rotterdam, and Amsterdam. The team hopes to be able to make recommendations on how such technology might be employed in the U.S. to dispose of solid wastes in such fashion as to produce steam that can be used to generate power.

No technology advance

When he was chief of the Office of Solid Wastes (PHS), Wesley E. Gilbertson, now director of environmental pollution control for Pennsylvania, made the following statement: "Because of the lack of research and development, solid waste disposal methods common throughout the U.S. today represent little advancement beyond the technology of the garbage pail, the trash can, the open dump, and the obsolete incinerator. The technological void which the national program was devised to fill is truly great. We must be prepared for a long-term effort to fill it."

In his dual role as a regional vice president of the National Society of Professional Engineers and chairman of the society's pollution control committee, Mr. Gilbertson observed: "Although specialized elements of engineering are active in pollution abatement, the engineering profession as a whole unfortunately has not developed

a positive posture with regard to control of environmental pollution." At a recent national NSPE meeting he read a report that castigated the engineering profession for having too often followed rather than led in the development of public policy with regard to the serious problem of control of environmental pollution.

Society is aroused, the professionals are responding, and the politicians are providing the incentive and the means.

Auto scrap

Mrs. Lyndon B. Johnson's beautification program has highlighted one aspect of the solid waste problem—the automobile graveyard. An estimated 6 million cars annually enter the scrap heap. At the White House Conference on Natural Beauty in May of last year, the Institute of Scrap Iron and Steel summarized the problem this way: "Old cars can't be buried, they can't be economically dumped into the sea, they can't be screened out of existence. They must be moved more quickly and in greater numbers into the consumption channel as scrap."

Walter R. Hibbard, Jr., director of the Interior Department's Bureau of Mines, adds a further thought: "Dealing with the mounting piles of scrap will demand the best skills of modern extractive metallurgy." Speaking last month at the annual meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers in Los Angeles, Dr. Hibbard noted that "Extractive processes can and should be developed for recovery of the metal values that these scrap materials contain. Above all, scrap heaps and other secondary sources must be considered on the same terms as conventional mines; in fact, the mineral values such sources contain often greatly exceed those of a natural mineral deposit."

BuMines has recently made a number of moves regarding automobile scrap. (Under the 1965 act, Interior deals with solid wastes associated with the production and use of minerals.) BuMines is now building a demonstration plant that will use automobile scrap—as well as other low grade ferrous materials—to convert a generally unused type of iron ore into blast furnace feed. The

\$4.5 million plant will be built between Nashwauk and Kewatin, Minn., where there are vast reserves of non-magnetic taconite. Roasting a scrap-ore mixture produces a magnetic iron oxide that can then be concentrated into blast furnace feed. The plant, scheduled to begin operation in 1968, will use up to 15,000 tons of scrap in processing 150,000 tons of ore annually.

The presence of copper in auto scrap is a major barrier to use of scrap in steelmaking. BuMines recently awarded a \$45,000 contract to Ralph Stone and Co., Inc., Engineers, to conduct two related studies of the copper contamination problem. The first objective is designed to determine relationships between the location and attachment of copper parts on automobiles and the costs incurred by scrap dealers in processing the cars. The second objective is to develop preliminary automobile-component design data aimed at simplifying the salvage of both copper and steel from scrap.

Mining wastes

BuMines has awarded a contract to the University of Wisconsin to find out if products useful in steelmaking can be obtained from large tonnages of zinc mining and milling wastes. These wastes are accumulating at the rate of nearly 2000 tons a day in Wisconsin's Upper Mississippi Valley zinc district. One possible useful product from these wastes is burnt dolomitic lime, which can be used as a flux in steelmaking. Other possibilities: iron oxide sinter for blast furnace feed and elemental sulfur. The university will characterize the chemical components of the waste materials, evaluate processing steps, and study potential markets in the Midwest. The grant is for \$27,399 to finance the first year of a 2½-year research program.

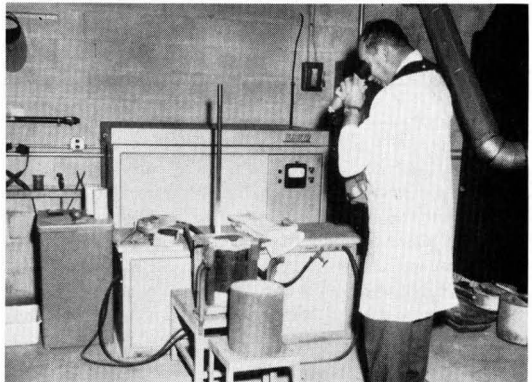
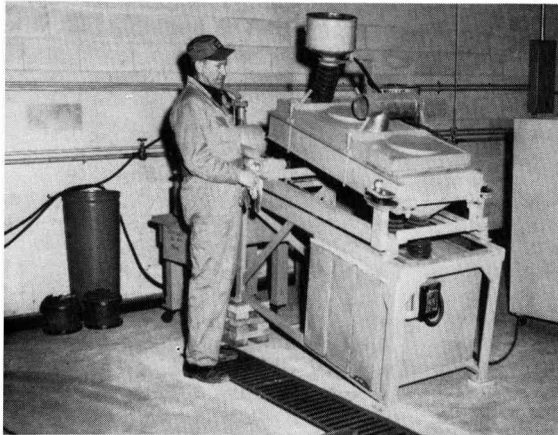
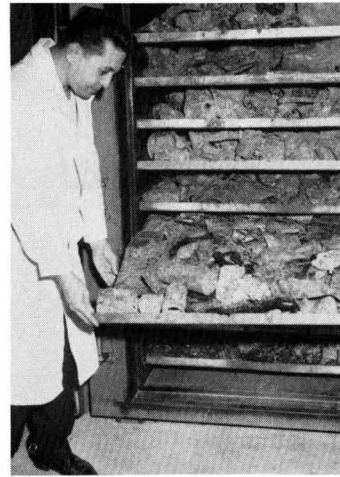
This grant, and other related ones, not only provide for R & D on immediate problems, but each grant also assists graduate students working for advanced degrees in some aspect of the solid waste disposal field.

Coal washery wastes

Under another BuMines contract, Franklin Institute (Philadelphia) will study the possibility of using the dusts

Waste Not, Want Not

The refuse that goes to the nation's incinerators is a potentially valuable source of minerals, and BuMines has an active R&D program to develop ways for efficient recovery and utilization of these materials. In pilot operations at BuMines' College Park, Md., facility, incinerator residue is sampled (upper left), sent to special drying ovens (upper right), then separated into various fractions (lower left). Nonferrous metals recovered from incinerator residues are melted in a furnace in a special recovery step (lower right)



generated in washing coal to improve the properties of concrete, gypsum, and other building materials. About 20 million tons of such dusts are produced annually; about half is recovered and sold, the remainder is discharged into settling basins, where it poses a pollution threat. Because the microscopic particles of coal dust are needle-shaped, they should effectively reinforce construction materials. Also, because the dusts resist moisture, they could help to make cement and other products more impervious to water. The two-year contract is for \$62,793.

Mine dumps

The landslide that took 145 lives last fall in Aberfan, Wales, renewed concern about the coal mine dumps in West Virginia, Pennsylvania, and Kentucky. These culm banks are a problem from the standpoint of environmental blight,

danger of fire, acid drainage into streams, and smoke and dust pollution of the air. The Interior Department has had these piles under surveillance for several years. Now, under terms of the Solid Waste Disposal Act, teams from Interior's BuMines and Geological Survey are intensifying efforts to find better disposal methods, as well as possible economic uses for the material in the culm banks.

The Commonwealth of Kentucky recently took action to halt the close-to-200 culm pile fires now burning within its boundaries. Under a \$100,000 contract, Melpar, Inc., will study ways of extinguishing the fires, which start spontaneously and discharge sulfur dioxide into the atmosphere and create other noxious effects. The fires are fed by oxygen penetrating voids or fissures in the residual coal and mine tailings. Melpar plans to use grouting

techniques, drilling holes in the piles and pumping in a liquid vermiculite mixture to fill the voids and cut off the supply of oxygen.

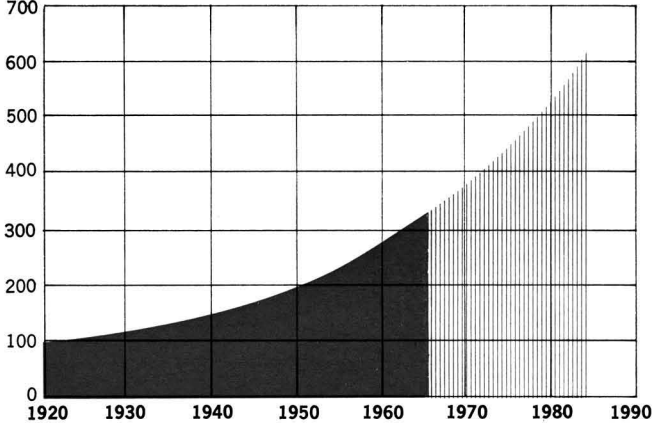
Fly ash

Burning coal creates still another problem—what to do with fly ash, the unburned mineral matter produced at power plants and other coal-burning installations. When it was discharged from smokestacks, fly ash was an air pollution problem. Now that it is trapped by collectors inside the stack, it is a solid waste disposal problem. As much as 20 million tons of fly ash accumulate each year at domestic power plants alone. Interior's Hibbard referring to this material, said: "We are throwing away a fortune every year, and paying dearly for the privilege." The U.S. uses only 4% of the fly ash generated annually, whereas France uses

Refuse production in the U.S. is rising rapidly

More than 300 billion pounds per year for the U.S. . . .

Billions of pounds



50% and Britain 40%. "Even the ancient Romans recognized the value of fly ash," Hibbard said. "They went out and gathered the ash from volcanoes and used it to make brick."

Fly ash offers important advantages to construction firms and manufacturers of building products. Concrete made with the proper proportion of fly ash is many times stronger than the ordinary variety and is less likely to shrink or crack when exposed to freezing and thawing, Hibbard pointed out. In concrete block, it helps give a more uniform

texture and sharper corners. The ash has the same beneficial effects on brick.

Fly ash could also be used to stabilize the soil under highways; it is a good filler for asphalt. It has possibilities for use as an abrasive, a soil conditioner, and a water clarifier in water treatment plants. Fly ash is frequently available in large quantities at relatively low cost near many metropolitan areas. With all these advantages, why are such small amounts used? "Because," says Hibbard, "the construction industry and others have not been properly educated";

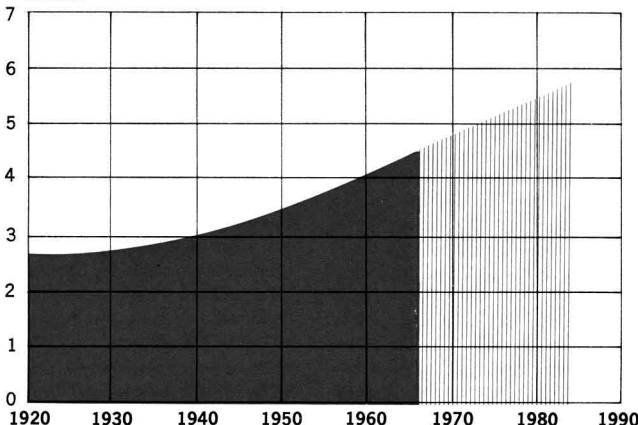
a situation his department is now trying to correct.

Interior is also trying to develop an economically feasible system for simultaneously removing sulfur compounds and fly ash from flue gases. BuMines has granted \$22,474 to Carnegie Institute of Technology (Pittsburgh) to finance the first year of a proposed three-year development program to help find such a system. Carnegie Tech seeks to find a solid material that attracts fly ash and absorbs sulfur compounds at reasonable temperatures. To accomplish this simultaneous removal, Carnegie proposes to use a shaft filter, a bed of slowly falling particles through which the gas stream passes horizontally. The absorbent material will have to be inexpensive, or a regeneration scheme will be needed. Also, Carnegie will have to determine if the fly ash interferes with sulfur removal.

The Army's Corps of Engineers has launched a nationwide program to prevent industry from depositing solid wastes into navigable channels. When complete elimination is not feasible, the Corps will try to have violators pay for dredging costs. Its program will include a study to develop techniques and criteria for determining the amount of suspended solids contained in industrial plant waste discharges. By law, the Corps has no authority over liquid wastes or the discharges from sanitary sewers, storm sewers, and sewage disposal plants, whether caused by natural drainage or erosion.

... And almost 5 pounds per capita per day

Pounds



Not too late

Although he was speaking about the problem of urban solid wastes, Mr. Gilbertson's remarks provide a good commentary on the solid waste problem in general. "... If these trends which we see and deplore are not to continue, then one of the problems we will have to learn to deal with is the problem created by the mismanagement of urban solid wastes. We have started this part of our practical education perilously late in the day, but not too late. I think we as a nation have begun to appreciate the full and growing significance of the solid waste problem at a time when our resources and energies are equal to the challenge. But time and the stupendous capacity we have to produce waste are working against us. There is only one best time to solve the solid waste problem, and it is now."

A Wild Fish Should Be Safe To Eat

The interaction of drinking water standards, stream water quality standards, and food standards

M. B. Ettinger and Donald I. Mount

Federal Water Pollution Control Administration, Cincinnati, Ohio

The promulgation of guidelines for establishing water quality standards for interstate waters by the Department of the Interior in May of 1966, positively affirmed that *the use of waters for propagation of fish* must be a consideration in any set of acceptable state water quality criteria. In this article we will discuss the implications of this requirement and show that it has a bearing on drinking water standards, and, in turn, that it is affected by food standards. Further, we will develop from this requirement maximum acceptable limits for chlorinated hydrocarbon pesticides in drinking water which are compatible with stream water quality standards as constrained by food quality needs.

We have assumed that it is the intent of Interior to protect fish, shell fish, and the food organisms which support the higher forms. This intention also has to mean that the fish or shell fish must persist not only as a standing crop, but that these biota must also qualify as an edible food resource.

The fish population of fresh water is wonderfully adapted to taking toxic material in water and concentrating it in body structure. At the top of the aquatic food chain, a fish can accumulate radioactivity many times greater than that in the water it inhabits. A fish also has an enormous capacity for direct concentration of organic material from the water it inhabits. Indeed, fishes concentrate certain organic toxicants, such as endrin, DDT, and toxaphene, by factors of up to 20,000. Although a

fish may be killed in water containing minute concentrations of such lethal agents, the fish is likely to show a high pesticide concentration even before its death removes it from the major food chain of man. Further evidence that concentration of lethal agents occurs in the food chain of fish is that older predator fish have the greatest pesticide concentration of all fish living in polluted environments.

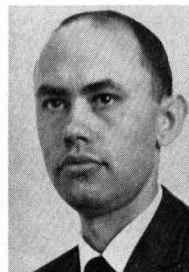
Water quality criteria for water supporting wholesome fish

A wild fish available for capture should also be a wild fish which is safe to eat. It should not have a potentially dangerous burden of radioactivity, toxic metal, or insecticide. Given a choice between survival of an unwholesome wild fish population and its disappearance, one must reasonably decide that no fish are probably better than toxic fish.

Fixing stream water quality standards which preclude the development of fish which are toxic is an attainable objective. Fixing standards for water quality which preclude the development of unpalatable fish is a much more difficult problem. Fish can concentrate many types of organic material from the water in the same way as chlorinated hydrocarbon pesticides are concentrated—and react to such concentration in a variety of patterns. Some materials concentrated by fish from the water in which they live are materials that are excreted, be it efficiently or inefficiently. Thus, a fish put in clear water purges



M. B. Ettinger

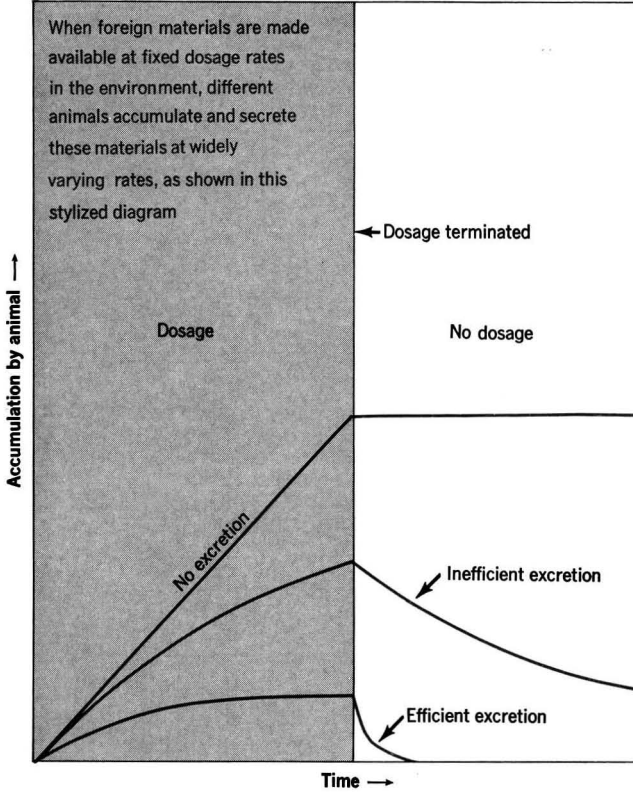


D. I. Mount

Morris B. Ettinger is a staff member, Office of the Director of Research, Federal Water Pollution Control Administration, Cincinnati Water Research Laboratory. A commissioned officer in the Public Health Service for 25 years, Mr. Ettinger has been awarded the PHS Meritorious Service Medal for outstanding achievements. He received his B.S. in chemical engineering (1933) from Washington University, and an M.S. in Chemistry (1934) at the same university. A Registered Professional Engineer of Ohio, Mr. Ettinger is a member of ACS, the Water Pollution Control Federation, and a Diplomat of the American Society of Sanitary Engineers.

Dr. Donald I. Mount is supervisor, Fish Toxicology Laboratory, Newton, Ohio, Federal Water Pollution Control Administration. A graduate of Ohio State University (1953), Dr. Mount received his M.S. in ichthyology (1957) and Ph.D. in aquatic physiology (1960), also from Ohio State University. He is a member of the American Fisheries Society, Wildlife Society, Ohio Academy of Science, AAAS, Sigma Xi, and Phi Eta Sigma.

Animals react differently to materials in their environment



itself of the foreign material previously stored. Effective use of this quality is involved in the well known practice in the Ohio River Valley—fish-for-pay lakes are stocked with fish taken from areas where they have been fouled organoleptically by materials in their habitat.

After a purge period in a different environment, these previously undesirable fish frequently become more acceptable to a consumer. Provided the fish are not toxic, there then appears to be some value in encouraging survival of unpalatable fish. The sporting value of fish is unimpaired and it provides the possibility of entertainment to the sportsman, even though he may be disgruntled to find that his catch has an obscene flavor. However, since the same materials which flavor a fish can also flavor drinking water, rational water quality objectives must seek to minimize such pollutants.

We have based our discussion of standards for toxic pesticides (chlorinated hydrocarbons) on two sets of guidelines:

- Fish can concentrate a toxic chlorinated hydrocarbon pesticide by a factor of as much as 10,000. (Presumably, much higher concentrations will sometimes be encountered where predation and food chain concentration are factors.)

- The lowest dietary level of pesticide which has been shown to have an effect on mammals is the minimum level acceptable in the habitat. However, this value at first glance probably needs to be hedged by a safety factor. But, since fish rarely reach 10% of man's dietary intake, we deem it unnecessary to provide a safety factor in our calculations. Instead, we rely upon the dietary composition to provide an acceptably small risk situation.

Accordingly, the physiological reference point should be divided by 10,000, the fish concentration factor. The resulting number, then, is the maximum concentration of the pesticide permissible in surface water which is expected to contain a harvest crop of fish. Application of this procedure to minimum response levels of animal toxicity prepared by W. J. Hayes (Advisory Committee on Use of the Public Health Service Drinking Water Standards—1965) leads to the values of acceptable pesticide concentrations shown in the following table:

Chlorinated hydrocarbon pesticide	Hayes' values for lowest dietary level with minimum effects on rats (parts per million)	Our values for maximum reasonable stream allowance ^a (parts per billion)
Endrin	1.0	0.1
Aldrin	2.5	0.25
Dieldrin	2.5	0.25
Lindane	50.	5.0
Toxaphene	25.	2.5
Heptachlor	10.	1.0
Heptachlor epoxide	10.	1.0
DDT	5.	0.5
Chlordane	2.5	0.25
Methoxychlor	200.0	20.00

^a (Hayes' minimum response levels divided by 10,000.)

In addition to the requirement that a captured fish shall not be toxic to man, there should be the requirement that the environment be suitable for maintaining a standing crop of fish—all of which demands fish survival, reproduction, and normal growth. Quality restrictions based on these considerations do, indeed, need to be considered for many of these 10 chlorinated hydrocarbons. Obviously, the fish species which does not survive or reproduce cannot present a toxicity hazard to a human consumer. However, it is not the purpose of this discussion to suggest quality standards related to fish production. Rather, we wish to consider here only the problem of toxic fish.

Drinking water standards and stream water quality standards

Drinking water standards cannot permit water plants to adulterate raw water with material that is toxic to man—or animals of interest to man. Ac-

cordingly, recommended standards for drinking water quality should be set so that they are not more tolerant than the standards governing the quality of raw water. This provision leads directly to one group of restrictions for suitable recommended drinking water standards for chlorinated hydrocarbons, namely those outlined in the accompanying table. We must also point out that the other water quality requirements might lead to even more restrictive values than those we have enumerated.

We do not mean to suggest that standards of drinking water quality such as we have developed are at the threshold of danger to the health of man in terms of water intake. What we do suggest is that a second set of standards (grounds for rejection standards) be derived, based on an entirely different set of considerations. Such a set of standards is presently being developed by a task force on toxicology established by the current "Advisory Committee on Use of the Public Health Service Drinking Water Standards Committee."

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QUOTE . . .

WATER FOR THE FUTURE

Planning water supply for the future implies some foreknowledge or forecast of future situations and water-supply needs. Some commentators advocate that planners should look ahead at least 100 years. The tempo of change is such that it is not possible to foresee the situation in 2067. It seems more important to do the planning and development in shorter terms but in such a way as to leave maximum flexibility for the future. Is it too much to expect that our descendants will have greater ability than we to cope with their problems?

Ideally, planning should enable us to bequeath to the next generation and development in shorter terms but in such a way as to leave maximum flexibility for the future. Is it too much to expect that our descendants will have greater ability than we to cope with their problems? Ideally, planning should enable us to bequeath to the next generation of people a world at least as good as the one we entered. Planning should not commit that generation to our own shortcomings....

...Three besetting sins tempt the planners and their advisers in a world in which science and technology are major social forces, in which size is a principal measure of importance, and in which the landscape is only something to be altered.

- Faith in science and technology.
- Worship of bigness.
- Arrogance toward the landscape.

...Seemingly, no important new physical concept of proved value in water management has risen in the last 600 years. The technology of dam construction has improved, for example, but the product is still just a dam. Purposes are unchanged: to alter nature's plumbing system in order to put water where someone wants it today, with only superficial thought about where our descendants may want it tomorrow.

...Human assumption that all nature exists exclusively for man's benefit bespeaks a degree of intellectual arrogance that is matched only by basic human ignorance of nature. This attitude is at the root of most of our troubles with the landscape. While man, in his self-imputed wisdom, works toward his own purposes, Nature reacts in accord with natural law, and the landscape bears the scars. If water shortage is a frame of mind, water planning for the future requires a changed frame of mind, not only among the planners but also among the water users....

...It seems essential that planners bring themselves up short and seek some new perspective in planning. The Nation is not short of water so long as 95% of its free-running supply runs off into the sea. However, we are bound to have recurrent apparent water shortages so long as 95% does run off....

...Planning for the future, therefore, should include much attention to more efficient and more effective use and reuse of water. In many cases this could eliminate or postpone the need for new or additional supplies. For example, management of ground-water reservoirs, as reservoirs, in distinction from their haphazard exploitation as wind-fall sources of water, is yet in its infancy

DR. RAYMOND L. NACE

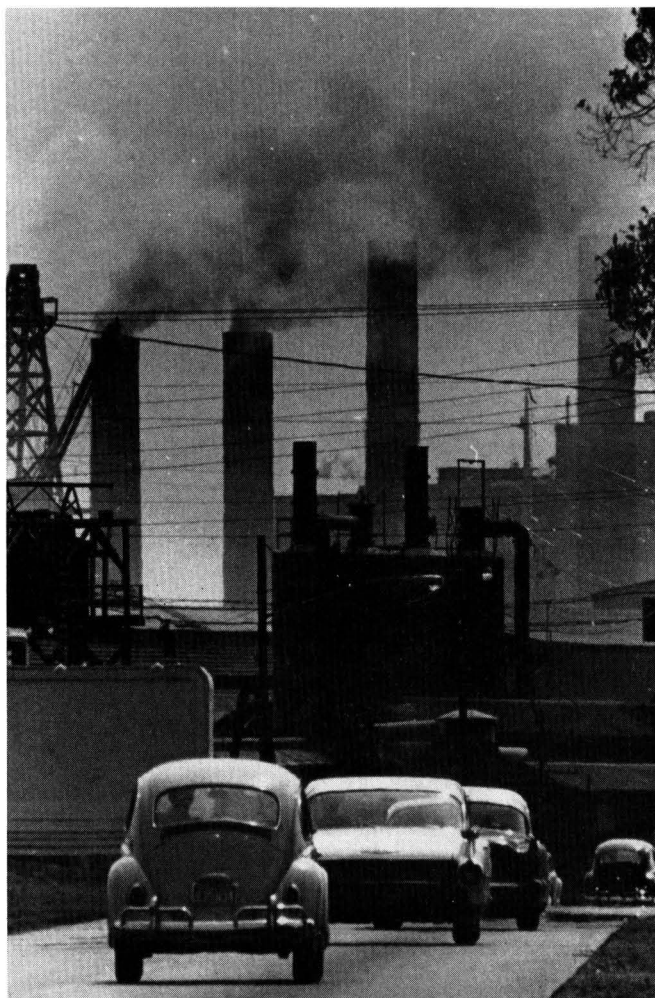
U.S. Geological Survey and Chairman of the U.S. National Committee for the International Hydrological Decade (1965-74) at the 35th Annual Meeting of the California Municipal Association, Sacramento, March 2, 1967

John T. Middleton

*Director, National Center for Air
Pollution Control, Washington, D.C.*

A Fresh Opportunity for Industry

With a set of air pollution standards, industry can make a reasoned and resolute response to the problems of air pollution. Without such standards, industry is shackled to the horns of a dilemma



Double-barreled. *Two major sources of air pollution at work simultaneously—smokestacks of the industrial plant and exhaust pipes of the automobile*

The proposed Air Quality Act of 1967 is an unprecedented opportunity for the business community to carry out its responsibility for controlling the growing problem of air pollution in this country.

I do not believe I have to start out by making a case for air pollution control. I think we are all too familiar with air pollution. And I think we are uncomfortably aware that in spite of the greatly expanded efforts to cope with the problem in the past few years, we are not catching up. Air pollution is getting worse, not better. We must come to grips with the problem now.

This was the feeling that pervaded the prepared papers and the open discussions at the National Conference on Air Pollution held in Washington this past December. Attended by representatives of business and labor, the scientific disciplines, industrial and civic organizations, and all levels of government, the conference thoroughly examined the complex problem that air pollution presents. Those who attended that conference, I believe, will agree with me that with all the diverse points of view, there was consensus. There was a great deal of discussion at the conference about just what steps should be taken to control air pollution, and who should take them. But there was no disagreement that whatever must be done should be done now.

A few days before the National Conference on Air Pollution here in Washington, a somewhat similar attitude was expressed at a meeting in Houston, Texas, by the president of the U.S.

Chamber of Commerce and chairman of the board of Humble Oil Refining Co., Mr. M. A. Wright. Mr. Wright said:

"We in business have only two alternatives. Either we voluntarily implement effective pollution abatement programs—at all levels of business and industry—or in the near future our actions in this area will be spelled out by Congressional legislation. Today, we still have the freedom to make a reasoned and resolute response to the problem; tomorrow our actions may be tightly controlled by government regulations. If our efforts in this area are made mandatory, not only will we be forced to take more costly and less efficient action, but we will also forfeit our claim to being a responsible segment of society. To those who say they cannot afford to take effective antipollution measures, I can only respond that they can't afford not to."

Industry's efforts

I am fully in sympathy with Mr. Wright's position on the need for industry to implement pollution abatement programs, and I can understand his fears for the future if industry fails to do so. However, I cannot agree that industry is today entirely free to make a reasoned and resolute response to the problem; and without that freedom I do not think it realistic to expect voluntary implementation of pollution abatement programs.

Let us for a moment take a look at what we have been asking of industry. It is common knowledge that in spite of the fact that the costs of the effects of air pollution are several times as high as the costs of adequate control, the operator of a source of pollution often has less

than adequate motivation to control it. Pollution controls ordinarily add to the costs of manufacturing, and do not add to the return on the product.

The operator, concerned about his competitive position, and seeking to minimize his costs and maximize his returns, is often motivated *not* to control pollution. And since under our present laws a state or a city that sets up an effective control program is more often than not asking its industries to take on a competitive disadvantage, the disinclination in industry boardrooms to control pollution is also felt in the chambers of government where there is understandable concern not only with the air citizens breathe, but also with the source of their employment.

Minimum national standards

If we accept this admittedly cursory analysis of the built-in conflicts which industry must resolve in this field it is apparent to me that what emerges is a clear need for air pollution standards which can be applied universally and equitably. Without such standards, industry is *not* free to make a reasoned and resolute response to the problem of air pollution but is shackled to the horns of a dilemma—it needs to maintain its place as a responsible segment of society, as Mr. Wright suggests, but it also needs to maintain its competitive position in the market place.

Emission standards

For industry to support the establishment of minimum national emission standards may seem a novel idea to some, but that is precisely the course that is indicated if industry is to extricate itself from this dilemma.

Dr. Middleton presented this talk at a U.S. Chamber of Commerce meeting in Washington, D.C., on February 28.

These are but a few of the reasons that I endorse the proposed Air Quality Act of 1967 as an unprecedented opportunity.

Under one of the major provisions of this act the Secretary of HEW would set emission standards for those industries which contribute substantially to the problem of air pollution, and which with reasonable efforts could substantially reduce or prevent pollution. In recommending this provision, President Johnson said:

"... emission control levels should be set for those industries that contribute heavily to air pollution. Today, no such levels exist. Industries do not know to what extent they should control their sources of pollution or what will be required of them in the future. Strong state and local standards—essential to pollution control—cannot be effective if neighboring states and cities do not have strong standards of their own. Nor can such local standards gain the support of industry and the public, unless they know that plants in adjoining communities must also meet standards at least as strict. We need the means to ensure comparable emission levels for a given industrial source of pollution throughout the country."

What these national standards would mean, in effect, is that those industries which everyone now admits to be a problem, wherever they are located, would be subject to regulations which would place them under the degree of control that current technology readily admits. I do not see how this can fail to be of direct benefit to those whose responsibility it is to control air pollution at the state and local levels of government, and I cannot see how this can fail to be of benefit to industry.

Control patchwork

The patchwork pattern of control, if a patchwork can be called a pattern,

which exists throughout the country today must frankly cause many managers and owners of industry a severe executive headache. A steel mill in one community located right in the center of town might still succeed in doing business while it freely emits particulate pollutants as if there were no technically economically feasible means of control available. Its competitor in a neighboring community might, because of the enforcement of state or local law, be forced to control these particulate emissions to a very high degree.

There is little justice in the situation I have just described, either for the people who breathe the pollutants in the first community or for the industry which controls the pollutants in the second community. Yet, the problems of obtaining adequate legislation and of obtaining the funds and the public support to control pollution in the first community may be almost impossible to attain for a great many reasons, some of which I have discussed. Federal emission standards as proposed in President Johnson's legislation would by no means clean up the country over night, but at least it would put us on the road to eliminating some of the gross inequities with which all of us, I am sure, are all too familiar.

Regional Air Quality Commissions

A second major provision of the proposed Air Quality Control Act would authorize the Secretary of HEW to establish regional air quality commissions in areas where pollution from one state endangers the health or welfare of persons in another state.

The task of developing control programs which transcend the artificial boundaries of our political divisions is particularly complex where two or more states are involved. Currently, under the 1963 Clean Air Act the only way an interstate program can be brought into

being is through the development of an interstate compact and its ratification, both by the legislatures of the states involved, and by Congress. In the three years since the Clean Air Act was adopted, only one such compact has come to Congress.

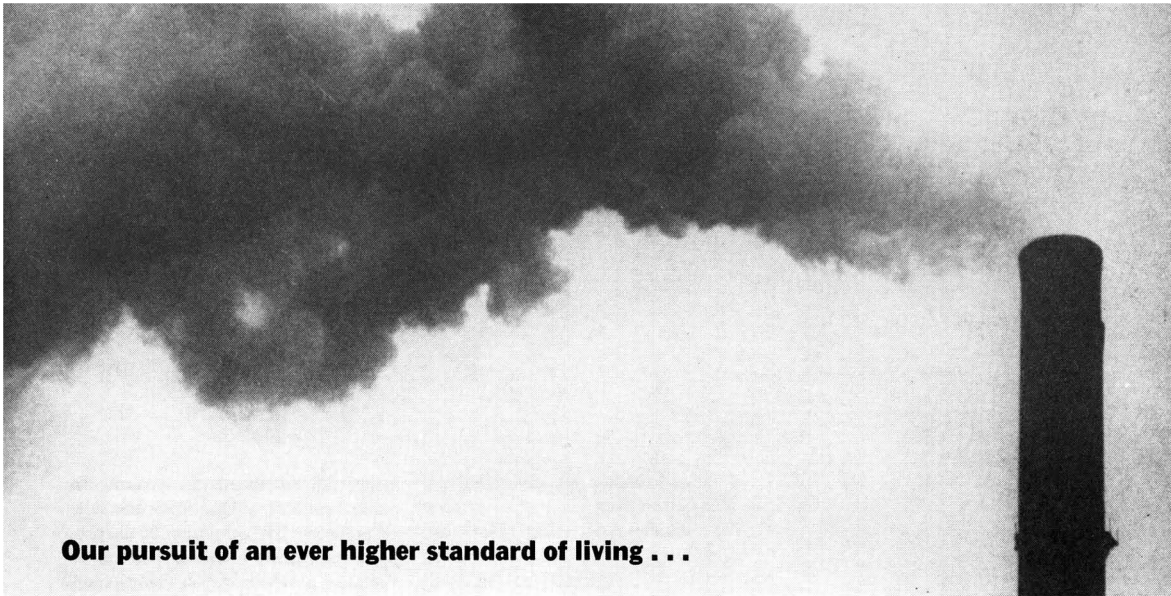
The proposed legislation would allow HEW to establish programs in interstate areas that would ensure that the problem could be dealt with on a political and economic basis that conforms, rather than conflicts, with the physical and scientific configurations of the problem.

At first glance it might appear to some that these two major provisions of the President's Air Quality Act of 1967 would diminish the role that states and local governments would play in the control of air pollution. If so, this first glance would be deceptive, for the fact is that under the President's proposed legislation the enforcement and control responsibilities of states and local governments would be greater, more meaningful, and more useful than they have ever been in the past.

Currently, the responsibility for setting emission standards for stationary sources of air pollution is assigned entirely to state and local governments. But, as I have pointed out, experience has proved that most states and cities will not take the initiative in requiring control measures beyond those required in other places; nor will industries support local or state control action which may place them at a competitive disadvantage.

Under the proposed Air Quality Act of 1967, the industrial emission standards set by the Secretary of HEW would apply only in those states which did not adopt standards that were equal to or more rigorous than the standards set by the secretary.

The same consideration applies to the regional air quality commissions, which would be established only in those interstate areas where states and local govern-



Our pursuit of an ever higher standard of living . . .

The major industrial contributors to air pollution in the U.S. are:

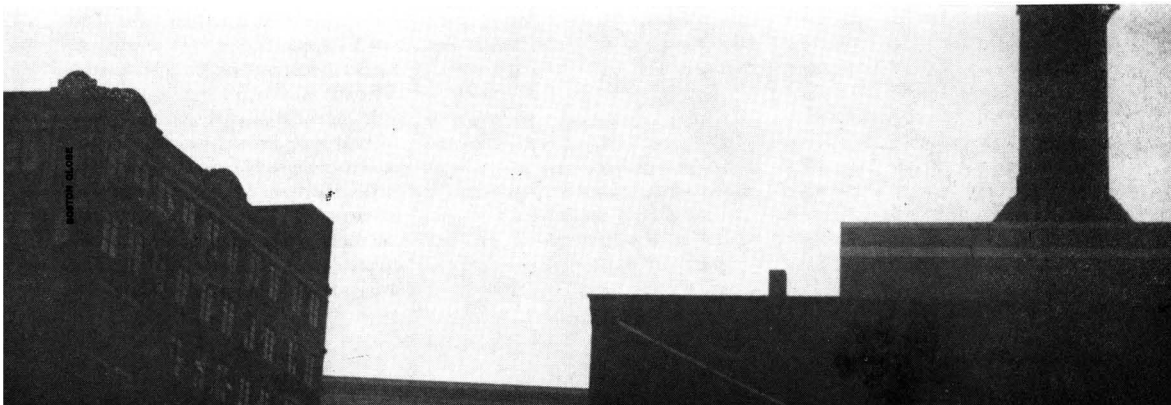
Inorganic chemical manufacturers
Iron and steel mills
Organic chemical manufacturers
Petroleum refineries
Pulp and paper mills
Smelters

Each year these industries discharge to the atmosphere

Sulfur oxides, 9 million tons
Particulate matter, 6 million tons
Hydrocarbons, 4 million tons
Carbon monoxide, 2 million tons
Nitrogen oxides, 2 million tons

Power plants add to air pollution, particularly the sulfurous contaminants

Sulfur dioxide, 12 million tons
Nitrogen oxides, 3 million tons
Particulate matter, 3 million tons
Carbon monoxide, 1 million tons
Hydrocarbons, less than 1 million tons



... Leads to pollution of the air we breathe

The fuel we use to heat and cool our dwellings and working areas releases

Sulfur oxides, 3 million tons
Carbon monoxide, 2 million tons
Hydrocarbons, 1 million tons
Nitrogen oxides, 1 million tons
Particulate matter, 1 million tons

Incinerating the mountain of refuse we generate each year creates

Carbon monoxide, 1 million tons
Hydrocarbons, 1 million tons
Particulate matter, 1 million tons
Nitrogen oxides, less than 1 million tons
Sulfur oxides, less than 1 million tons

Source: Public Health Service

ments fail to adequately protect the public health or welfare from interstate air pollution. This provision of the proposed Air Quality Act would place states and local governments, in many places for the first time, in a position from which they could successfully attack the problem they share in common.

Local involvement

Although all the details have not been worked out, it is clear that a commission established under the proposed legislation would not deprive states or local governments of their control and enforcement responsibilities. The commission might, indeed, establish guidelines or standards which the state and local governments in the region would not only be expected to contribute to, but would be expected to conform to. However, the only right such coordinated action might violate is the right of any governmental jurisdiction in the region to fail completely to control air pollution.

The commission would, on the other hand, provide all the citizens and industries in the region with the right to control resources of pollution with assurance that other jurisdictions and industries in the same region would do the same. The commission would put an end to the feelings of futility which now interfere with the control actions of both industry and governments who find that their efforts are in large measure wasted because their neighbors, who share the same regional air supply, fail to make commensurate control efforts.

Local jurisdictions would still be expected to qualify for grants assistance to develop their control programs and to carry out related enforcement and control activities. States would still be expected, as they are today, to develop strong programs, provide backup for

the communities within their jurisdictions, and to directly control sources of pollution where local efforts have failed. The formidable weight of responsibility which federal air pollution legislation has always left on the shoulders of state and local officials would remain there. The opportunity of successfully discharging this responsibility would, however, be improved.

Every other provision of the proposed new legislation will also help to improve the climate for an effective attack on air pollution problems. One such provision would pave the way for state inspection of motor vehicle pollution control equipment installed to comply with federal standards.

Fuel additives

Also proposed in the new legislation is a requirement that fuel additives be registered with the Secretary of HEW. This proposal is intended not to impose arbitrary restrictions on the use of such materials, but rather to provide opportunities for preventing the development of new pollution problems. This nation can no longer afford to wait years after the introduction of new materials to evaluate their effects on the environment and human health. The registration requirement will make it possible to evaluate fuel additives before their use has become widespread.

The final provision of the proposed Air Quality Act that I would like to comment on, and one that also provides a substantial new opportunity for the business community, would authorize federal financial support of public or private development of new or improved air pollution control methods. The development of new processes is almost always costly, time consuming, and sometimes frustrating, since failures occur more often than successes. In the

field of air pollution control these obstacles are often seen as insurmountable, since the incentive to overcome them, namely increased profits, may be insignificant or nonexistent.

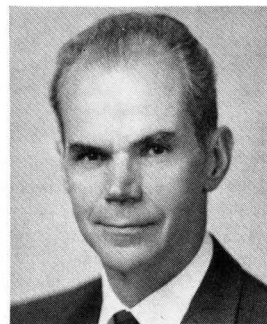
Mutual goal

The proposed new provision in the Air Quality Act would authorize HEW not only to work more effectively with trade associations and industry-wide groups, but also to work with individual industrial organizations. Under this provision of the act, federal funds could be used, for example, to construct a process demonstration plant on private property, operated by private management. This provision, in my opinion, is eminently reasonable. Developing a process at one site on behalf of all segments of an industry is the most economical way of achieving a mutual goal.

Our goal is a mutual one. As President Johnson said:

"It is in private laboratories, and in private boardrooms, that the crucial decisions on new fuels, new control technology, and new means of developing power and locomotion will be made. We should support private efforts now to expand the range of their alternatives and make wiser choices possible.

"The Government's relationship with private industry in this field should not be one merely of regulator and regulated. Pollution affects the lungs and eyes of worker, manager, owner, and government servant alike. The air cannot be divided into convenient shares. It is indivisible—and either clear and beneficial—or fouled and dangerous for all of us. Out of personal interest, as out of public duty, industry has a stake in making the air fit to breathe. An enlightened government will not only encourage private work toward that goal, but join and assist where it can."



Dr. John T. Middleton, director of the National Center for Air Pollution Control, was professor and director of the University of California Statewide Air Pollution Research Center at the time of his appointment to the newly created National Center on January 1. He received his B.S. from the University of California in 1935 and his Ph.D. from the University of Missouri in 1940. Dr. Middleton has served as chairman and member of the California Motor Vehicle Pollution control board since 1960 and on the Governor's Interagency Committee on Air Pollution and the Executive Task Force on Waste Management. He has served as consultant to many U.S. Government groups and to several European and American governments. Dr. Middleton, among his many other professional associations and societies, lists the Air Pollution Control Association, American Chemical Society, American Association for the Advancement of Science, Netherlands Plant Pathology Society, and Sigma Xi.

Lake Erie

DYING BUT NOT DEAD

Polluted tributaries and inshore waters, an open lake of high quality water sitting atop a bottom seriously fouled and getting worse—this describes the complex situation in what was once the most productive of the Great Lakes. But, as a paraphrase of Mark Twain might go, "The reports of its death are greatly exaggerated." There still may be time for man to hold back the dying process

According to the Cassandra interpreters of the score and plot, Lake Erie is dying in a not-so-funny drawn-out comic opera fashion. As the story goes, the villain, a hydra-headed thing comprising municipal sewage systems, ships and weekend boaters, industrial plants, and Mother Nature, is sadistically badgering the victim and generating an emotional storm amongst the onlookers and friends of the family. On stage now: the press-public-scientist monied-government multihero who, at least at this moment, believes he can pull off the old resurrection-of-the-Princess-of-the-Lake-trick. And well he might; he has been very exercised of late.

This month, for example, the Federal Water Pollution Control Administration convened a meeting of the continuing Federal-state enforcement conference on abating pollution in Lake Erie. In this, the first session, bordering states of Indiana, New York, Ohio, and Pennsylvania will present their programs for controlling pollution in the Great Lakes. Almost a year ago, Michigan submitted its program, which was approved by FWPCA.

Also this month, FWPCA-convened meetings were held in Chicago to discuss progress on efforts by Indiana, Illinois, and the City of Chicago to reduce pollution in Lake Michigan and its tribu-

aries. And coming this summer at the University of Wisconsin is an international symposium that will focus attention on the worldwide problem of the aging of lakes and streams. At this June meeting 36 scientists from the U.S., Canada, Japan, and several countries in Europe will discuss the scientific aspects of the aging of lakes, the social and economic consequences of such aging, and public policy in such matters.

From these conferences, from the many that have already taken place, from scientific studies and surveys completed, in progress, and planned, may come effective programs to prevent, for a time, the apparent geologically imminent death of Lake Erie with its subsequent deleterious effects on the four sister lakes and the surrounding land.

Natural aging of lakes

The key word in all these studies is eutrophication—an aging process brought about by an increasingly high level of lake fertility and the consequent rapid rate of growth of algae, fish and other animal life, and rooted aquatic plants—the natural and gradual aging process that occurs in all lakes and streams.

A lake begins as a body of cold, clear, almost sterile water. Streams from its drainage basin soon bring in silt, which

settles to the bottom, and nutrients, which encourage the rapid growth of plants and animals. As aquatic organisms increase and organic deposits pile up on the lake bottom, the lake gets smaller and shallower. The water gets warmer; plants take root in the bottom and gradually take over more space. The lake becomes a marsh, bog, and, finally, dry land. It's a natural phenomenon. But man in both his enterprise and naivete can alter the rate, which means, usually, that he brings about a rapid increase in the rate at which the lake ages—eutrophication.

Consider, for a moment, a lake which during the summer months has hundreds of square miles of bottom waters that are an aquatic desert. No fish and few invertebrates live there, a condition that has a dramatic and damaging impact on the fish population of the entire lake. Facing extinction in this lake are the lake herring, the blue pike, and the lake whitefish.

This is the picture of Lake Erie, a lake that is dying, but not yet dead, a picture painted by J. W. Moffett, J. F. Carr, of the U. S. Bureau of Fisheries, Ann Arbor, Mich., and L. L. Kempe, University of Michigan, Ann Arbor, at the annual meeting of the American Institute of Chemical Engineers in Detroit late last year.

Slowing the process

Lake Erie is young, geologically speaking, and there is much man can do to reduce the rate at which it is aging, just as he can slow the rusting of steel or the rotting of timbers. We are faced not so much with a *yes* or *no* problem, but rather with control of the rates of some of nature's own processes, Moffett and his colleagues noted.

Young though it is, Lake Erie is in a fairly advanced stage of eutrophication, the natural and gradual aging process all lakes undergo. Natural eutrophication is a slow process. But the record of the lake for the past 50 years shows that man's activities can greatly accelerate this process.

What has happened—and is happening—to Lake Erie is due to the expanding population (now more than 10 million) and industrial development in its basin. This acceleration of the natural eutrophication process is the basis to understanding the problems of Lake Erie.

The broad outlines and importance of the eutrophication process are generally agreed upon, but the mechanics in a body of water as large as Lake Erie are poorly understood. A better understanding of these causal mechanisms will not only lead to practices that slow down eutrophication, but will also help develop practical solutions to the lake's overall water quality problem.

Two categories

The water quality problems of Lake Erie can be placed in two categories:

- Tributaries and certain inshore areas.
- Open waters.

The most obvious degradation of water quality in Lake Erie has taken place in the tributaries and certain inshore areas. Swimming and water skiing have been curtailed because of high bacterial counts and dead plants, fish, and debris on the beaches. Some species of fish have died out; the flesh of others now have an undesirable taste.

These conditions are directly caused by water pollution, which arises from two principal sources—the Detroit River which empties into the lake, and the industrial and urban development around the lake itself. Waters from the river contain large quantities of sewage organics, bacteria, phenols, iron, oil, ammonia, chlorides, nitrogen compounds, phosphates, and suspended solids.



THE GREAT LAKES AND POLLUTION

The five Great Lakes are the greatest reservoir of fresh water in the world. Together they cover 95,200 square miles and contain 5457 cubic miles of water. In the southern part of the basin, from Milwaukee to Quebec, is a string of cities approaching the size and complexity of a megalopolis. In the minds of some economists, the industry and population of the Great Lakes region will become the fastest growing in the U.S. The reason: a seemingly inexhaustible supply of water. This forecast is restrained by the threat of pollution. Only in Lake Erie has pollution reached a serious stage, but three of the remaining lakes show the effects of pollution. Each exhibits its own pollution pattern, depending on both man and nature. Total dissolved solids are a good indication of this pollution:

Lake Superior (the largest fresh water lake in the world) sits up on the Canadian shield with very few people around it. The total dissolved solids have been practically constant since observations began.

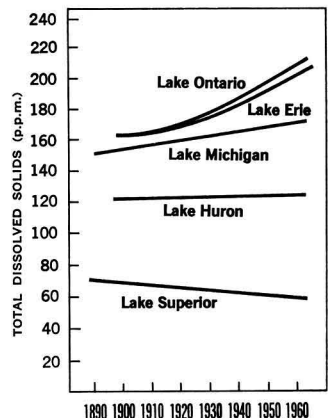
Lake Huron, bordered by a comparatively small population, so far shows only minor pollution effects. The modest increase in its dissolved solids is explained by the fact that it receives about 30% of its inflow from Lake Michigan, which is more heavily polluted.

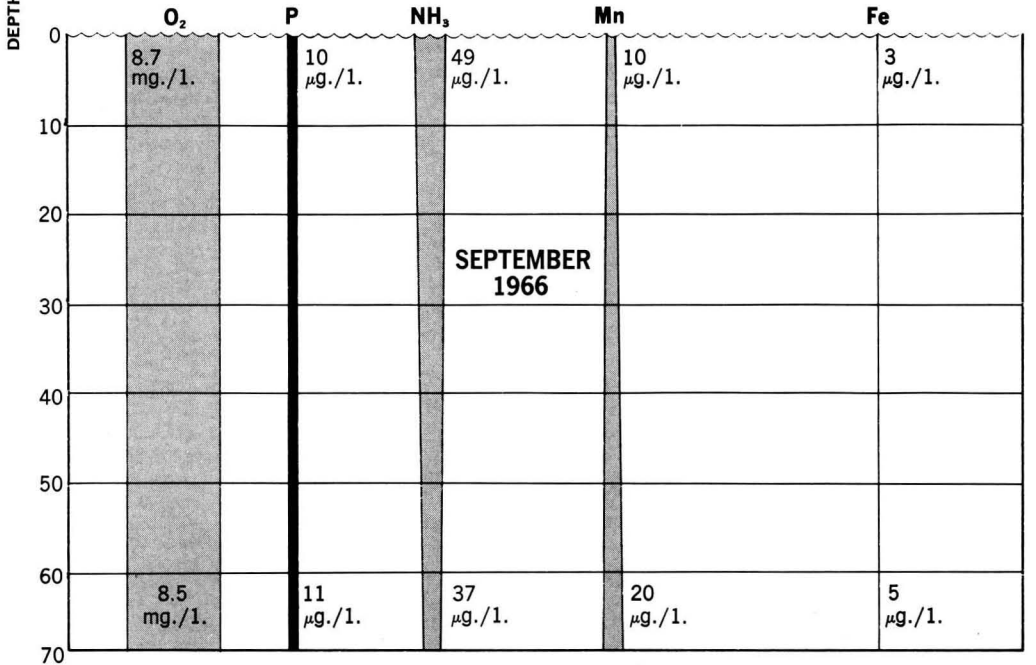
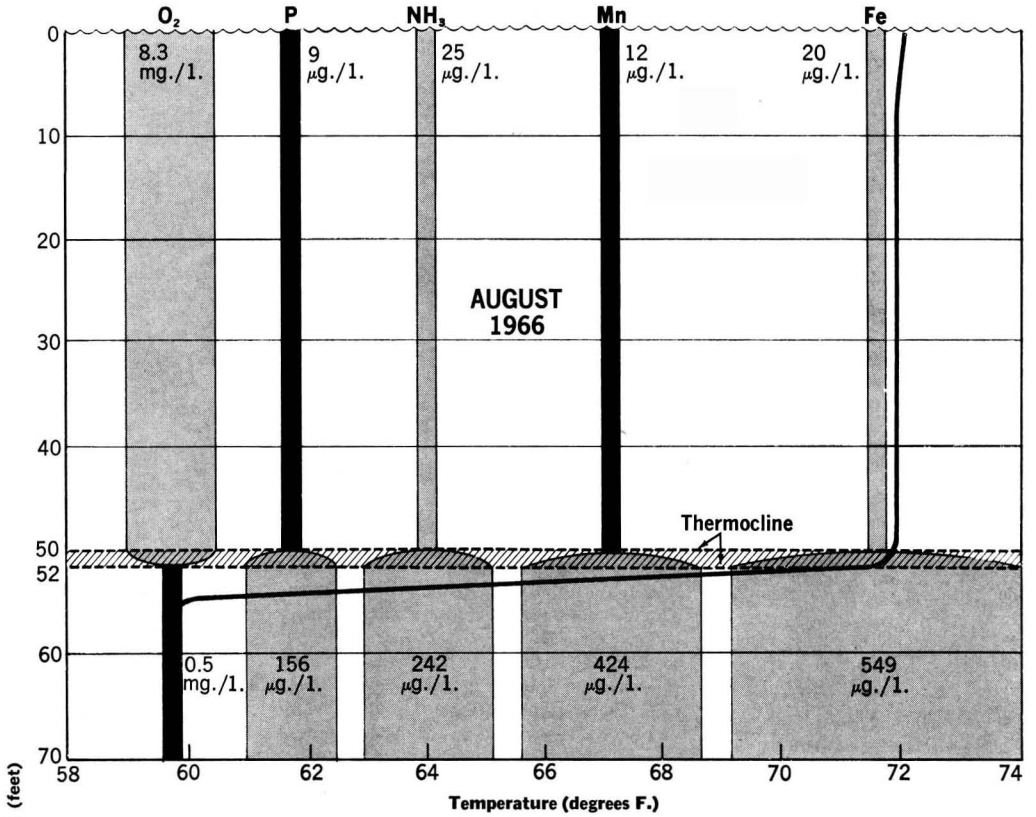
Lake Michigan is heavily polluted at the southern end, the main discharges coming from the large industrial concentration. (The area's major city,

Chicago, contributes little to lake pollution; it discharges its sewage into the Mississippi River system.) Aside from the southern end, the water of Lake Michigan is still of fairly good quality.

Lake Ontario receives a considerable discharge of waste, but the situation is not yet as serious as in Lake Erie. Lake Ontario has a much larger volume of water and so does a better job of diluting the pollutants. (The mean depth of Ontario is 283 feet, of Erie 58 feet.) Lake Ontario's pollution is a combination of what it receives from Lake Erie and from the cities along its shore. The greatest increases have been in chloride and sulfate, both of which are conspicuous in domestic and industrial wastes.

Dissolved solids in Great Lakes' water keeps rising overall





Thermal effects. During the summer months, thermal stratification occurs—the upper water layer to a depth of 52 feet is effectively separated from the lower water. During this period, the bottom layer becomes almost anaerobic and interesting chemical changes occur in this water layer as various materials begin to appear in appreciable concentration. When fall comes, the layering situation disappears and the waters take on a relative uniformity in the lake profile

Industries along the lake discharge similar waste materials. Aggravating the lake's pollution problem is shallowness—Erie's volume of water isn't big enough to dilute the pollutants effectively. Many of the industrial pollutants, particularly phenols and ammonia, are poisonous to fish and other animals.

The long range prospects for improving water quality in localized tributary and inshore areas are good, largely because of the water quality standards program now under way. The open waters of Lake Erie, on the other hand, pose different problems. Most of these waters are presently adequate for many human needs—municipal and water supplies and most industrial uses. For example, if the water quality is not adequate, it can still be made so by relatively simple and inexpensive treatment measures.

To understand what has happened and what may happen in the open lake in terms of water quality, one must turn to the fish and aquatic organisms, say Moffett, Carr, and Kempe. Some water quality factors such as color and bacterial count, are important to human and industrial users but unimportant to fish and aquatic organisms. But in general, the effects of subtle, sometimes intermittent, changes in water quality are felt first by fish and aquatic organisms.

Lake Erie is a case in point. In the mid-1950's scientists at the Interior Department's Bureau of Commercial Fisheries warned that major adverse changes were taking place in the total Lake Erie environment. These early warnings went largely unheeded.

Thermal stratification

One of the main changes has been in temperature, according to Moffett and his coworkers. The mean annual temperature of Lake Erie from 1926 to 1960, has increased by 2° F. This increase follows a general warming trend in the climate of the region. The temperature increase has accentuated thermal stratification, a condition that has always existed in deeper areas of the lake.

In August, for example, water temperature can be 72° F. at the surface and to a depth of about 50 feet. At 50 feet there is a marked temperature decrease to about 60° F., that occurs within only a few feet. In some areas, the temperature can change 13° F. in a one-foot change of depth.

Thermal stratification leads to the effective isolation of the bottom water from the top layer. Cut off from the air by the absence of convective mixing, the bottom water soon becomes depleted of dissolved oxygen. When the oxygen is consumed, it is not replenished until the thermal gradient disappears in the fall. Water which can hold 10 or 11 p.p.m. of dissolved oxygen contains less than 1 p.p.m. over hundreds of square miles.

This summer oxygen depletion is of overriding importance in its effect on aquatic life. When it occurs, it brings on major ecological changes. Bottom organisms and fish associated with that area have to clear out or die, according to Moffett, Carr, and Kempe.

Survival of the fish is threatened at other stages, too, since the eggs of all Lake Erie fish, except the fish-water drum sink to the bottom, where the eggs hatch and the young live for a while after hatching. Food sources change, too—mayfly nymphs, once a prime fish food on Lake Erie, have decreased drastically, for example.

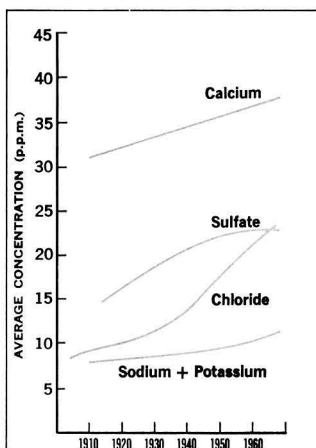
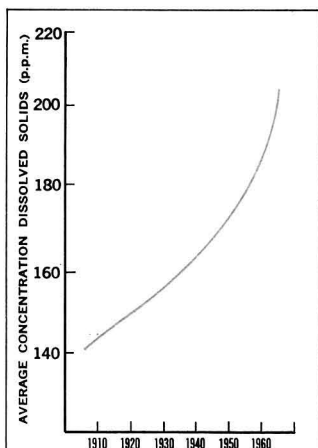
The reasons for this oxygen depletion are not clear. In the usual sequence, nutrients enter the lake from natural runoff and municipal and industrial waste sources. These nutrients serve as food for algae which subsequently die, sink to the bottom, and decay; large quantities of oxygen are consumed in the decay process.

Nutrients in the water

The oxygen depletion cannot be fully explained by direct transference of nutrient inputs into plankton-caused biological oxygen demand. If the fallout of plankton cells were the primary source of oxygen demand, the problem could be solved by reducing the input of nutrients. Reducing the amount of phosphates would be particularly important, since they are considered the prime stimulation to the growth of aquatic plants and plankton.

Reducing the nutrients poses technological problems. Many of the sources of suspended solids are uncontrolled—agricultural runoff, silt from cleared subdivisions, and residues from secondary sewage treatment plants, for example. Recently proposed water quality

Chemical content of Lake Erie waters continues upward climb



standards may have some effect in alleviating this nutrient charging.

However, really effective control could only result from complete exclusion of nutrients from surface waters. At present even the best sewage treatment processes remove only part of the carbonaceous biological oxygen demand; they do essentially nothing to remove such enriching nutrients as nitrates and phosphates.

Complete exclusion

Complete exclusion of even treated sewage and industrial wastes from surface waters is desirable, note Moffett and his coworkers. This exclusion can be accomplished by waste-water regeneration, permitting its reuse for industrial and domestic water supplies. Reuse is the logical way to protect fresh water lakes and streams from damaging effects of accelerated eutrophication caused by sewage and industrial wastes.

Present knowledge indicates the oxygen-demanding materials in the bottom sediments come from a variety of sources—not just plankton fallout—and have been accumulating in the sediment for many years. The problem appears tied to a complex set of relationships associated with the bottom sediments, including chemical as well as biological oxygen demand, Moffett, Carr, and Kempe observed.

When the thermocline is established during the summer months, some very interesting, though baffling, chemical phenomena occur. In the anaerobic conditions (less than 0.5 mg./l.) beneath the thermocline, soluble forms of phosphorus occur in the water system at a

level of 150 micrograms per liter, ammonia at 242 micrograms per liter, manganese at 424 micrograms per liter, and iron at 549 micrograms per liter. Above the thermocline, where dissolved oxygen is close to 8.3 mg./l., these substances occur at concentrations of between 9 to 25 micrograms per liter.

When the temperature gradient disappears, the high concentration of materials in the lower region also disappears. One thing that happens is that these materials become reoxygenated and precipitate. Another thing that happens is the rapid uptake of these materials by biological systems that use these materials very rapidly, often leading to a familiar phenomenon, the plankton bloom, Moffett and his colleagues observe.

Dissolved solids

Another of the long-term changes taking place in Lake Erie is in the quantity of dissolved solids in the system. The concentration increased gradually until about 1910, after which the rate of change accelerated. In the past 50 years the following changes have occurred: calcium, up 8 p.p.m.; chloride, up 16 p.p.m.; sodium and potassium, each up 5 p.p.m.; and sulfate, up 11 p.p.m. The differences are not realistically attributable to improved analytical techniques—Lake Superior has maintained a stable concentration since the observations first began, Moffett, Carr, and Kempe said.

These elements at these concentrations do not directly affect fish or aquatic organisms. Still, they are, in themselves,

a good index of pollution—they suggest the buildup of other substances for which good long-range data are not available, observed Moffett, Carr, and Kempe. Very little is known, for example, of the possible accumulation of toxic substances such as pesticides, detergents, and heavy metals in the waters, sediments, fish, and fish food supplies. Nor is much else known about the buildup of nitrogen and phosphorus, except that they are, indeed, building up in the lake.

Biological changes

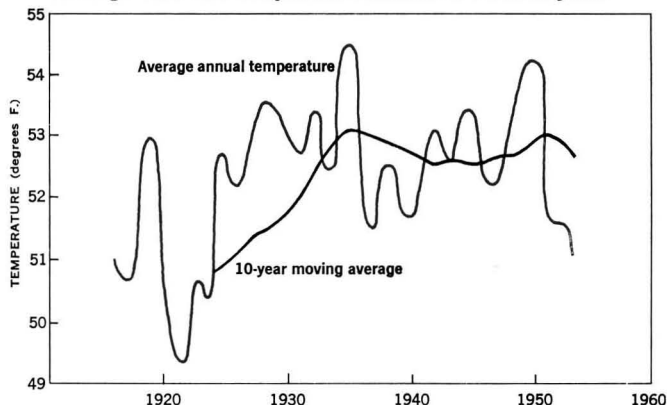
Lake Erie has been the most fertile and productive of all the Great Lakes. During the past 150 years, more than 15 fish species have contributed to the annual commercial fish harvest. Combined U.S. and Canadian fish harvests from Lake Erie have fluctuated little in the past 50 years, averaging about 50 million pounds annually. This production—most of it from the open lake—equals the combined production of the remaining four Great Lakes, according to a recent report on commercial fisheries resources of the Lake Erie basin by the Bureau of Commercial Fisheries.

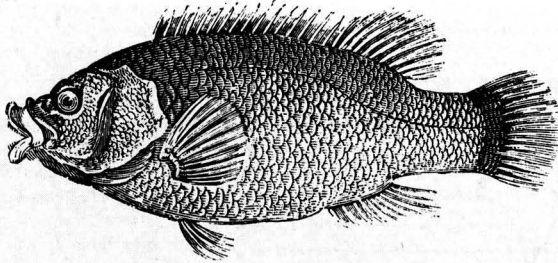
(Fish harvest increased markedly between 1951–60 largely because of the wide use of the efficient gill nets.)

The chemical and physical changes in Lake Erie in recent years have brought dramatic changes in fishing production—not in pounds, but in composition and value, the report states. (The sea lamprey has not been an important problem in Lake Erie, because few of the tributaries offer suitable spawning conditions for the lamprey.) Species once highly prized have virtually disappeared from the catch—the whitefish, cisco, blue pike, sauger, sturgeon, and northern pike. The first four are in imminent danger of biological, as well as commercial, extinction.

Walleye and yellow perch now are the major remaining species of higher and medium value. But stocks of these species are starting to decline and show signs of difficulty in perpetuating themselves. The less valuable species such as sheepshead, white bass, carp, suckers, smelt, and bullhead are still abundant and in some cases are increasing. Altogether, these changes in species composition have reduced the value of the catch by about \$6 million annually, according to the Bureau of Commercial Fisheries' report.

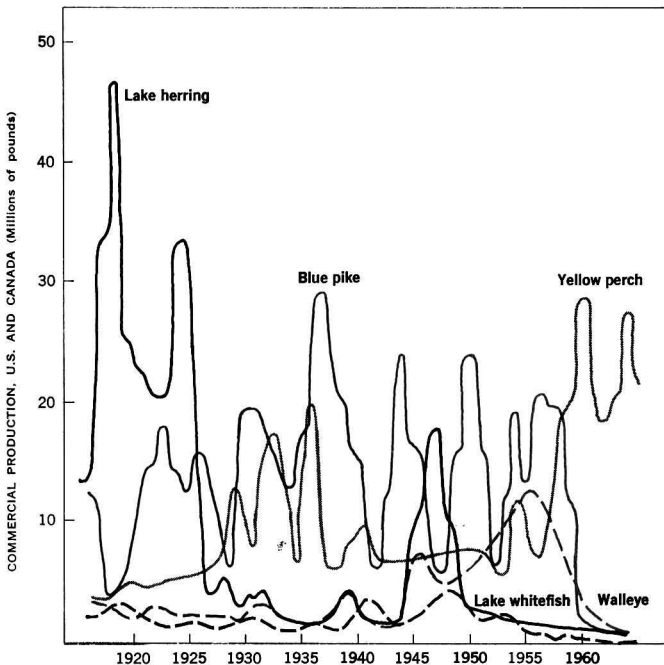
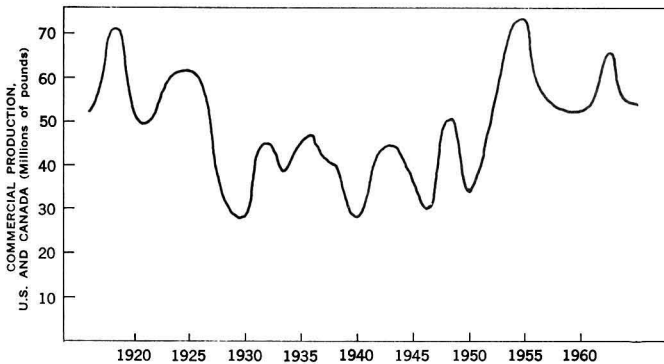
Average Lake Erie temperature climbed 2° F. in 30 years





Source: Thomas Bewick. *A Memoir of Thomas Bewick, Written by Himself. Embellished by Numerous Wood Engravings, Designed and Engraved by the Author for a Work on British Fishes, and Never Before Published.* London: Longman, Green, Longman, and Roberts, 1862.

Fish harvests in Lake Erie have changed in both kind and amount



Focus of research

Pollution abatement efforts currently under way promise direct and immediate benefit, particularly in the tributaries and inshore waters of the Lake Erie basin. But much more is needed. According to the "Report on Commercial Fisheries Resources of the Lake Erie Basin" research to save the open waters must focus on two areas:

- Development of specific water quality needed for fish.
- Determination of the specific causes of oxygen depletion.

Such a program should start with continuous measurement and evaluation of basic environmental features of the lake. The report contends that the program should extend to the tributaries, to the sources of domestic and industrial pollution, and to the physical and chemical processes within the lakes which concentrate, add, or remove material. Such information would provide the background needed to interpret and predict fluctuations and trends in fish distribution and abundance.

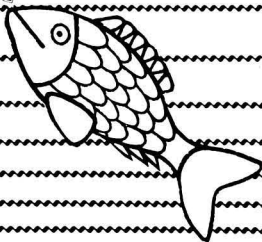
More knowledge is needed on the requirements of bottom organisms, which are consumed by almost all fish at some stage of their lives, the report points out. The scarcity of certain species may significantly affect the growth and survival of fish. Bottom organisms are also useful indicators of subtle physicochemical changes in water quality.

Bottom sediments hold the key to the long-range improvement of water in the Lake Erie ecosystem. According to the report, a sound plan for research on bottom sediments should involve:

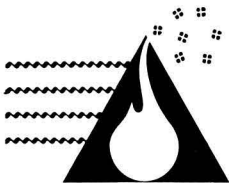
- Measuring the rate of sedimentation.
- Determining the amount of oxygen needed to oxidize the new sediment.
- Identifying the components of the new sediment.
- Calculating the total oxygen to stabilize the sediment and the oxygen deficit in Lake Erie.

An integral part of these studies would be the role of bacteria as the causative agent in producing chemical changes in both the overlying water and in the sediment. The transformation of organic matter in the Lake Erie basin must be studied, as must the rates at which it is synthesizing and decomposing, and the microorganisms and mechanisms involved in the decomposition; and the nature of the resulting products must be determined, the report says.

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More research is needed on bacteria as key organisms in the cycling of oxygen, nitrogen, phosphorus, iron, and carbon through the ecosystem. Related to the studies of the chemical cycles is a study of the chemical composition of the sediment and water with respect to their suitability (as a medium) for supporting the growth of bacteria. The chemical constituents which are of primary importance to bacterial growth are inorganic nitrogen sources (nitrate, nitrite, and ammonia), organic nitrogen, phosphorus (dissolved and combined), carbohydrates, and amino acids.

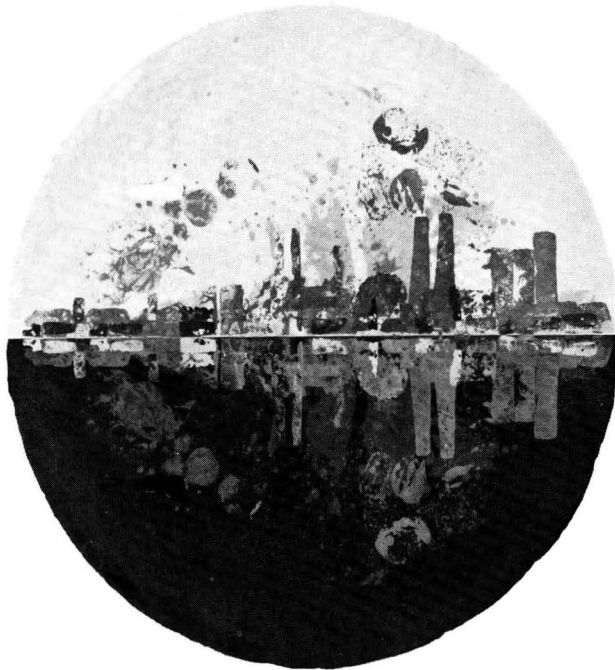
And, lastly, the report points out, plankton productivity should be determined, since plankton organisms are the most important primary converters of basic energy and nutrients in the deep waters of the lake.

Eutrophication

Lake Erie's rapid eutrophication is by no means unique. The classic example is the lower basin of Lake Zurich in Switzerland. The large amounts of human pollution it receives have moved the basin from youth to old age in less than a century. Lake Washington at Seattle is aging rapidly, as are the Yahara Lake chain in Wisconsin and Fure Lake in Denmark.

Moffett, Carr, and Kempe summed it up pretty well in the following manner: The biological productivity of a lake depends upon the presence in the water of substances essential to life. It is, however, important to recognize that all of the biological species have a maximum as well as a minimum requirement on the concentration of substances in the water. Once these maximums are exceeded, they are just as limiting to a species as if the substances were not there at all.

It has always been the history of increasing pollution, Moffett and his colleagues note, that fish are gone from further consideration long before man needs to do much about his water supply as far as its quality is concerned for his own drinking purposes. What these studies about the changes in the Lake Erie ecosystem mean is that it is high time for us to improve our technology so that the situation does not get to the point where we have to worry about water quality from a health standpoint or from limitations on its use in industry. The people around the Great Lakes must do something about arresting these unfortunate trends.



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i. Little, C., Locky, C., Lurkey, T., et al.,
in English Fairy Tales, David Nutt, London, 1890.

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Formation of Polysilicates as Determined by Coagulation Effects

Werner Stumm, Heinz Hüper, and Robert L. Champlin

Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass.

■ The solubility characteristics of amorphous silica are described by its solubility equilibrium with orthosilicic acid and monomeric and simple multimeric silicates. Polymeric silicates can be prepared by bringing sodium silicate solutions or soluble silica glasses temporarily into the pH-concentration range of oversaturation with respect to amorphous silica. The formation of polysilicates is detected by their effect on the stability of Al_2O_3 and AgBr sols. The coagulation method can be used to evaluate the various parameters that influence the surface chemical activity of polysilicates. Polysilicates at very small concentrations [$Si_T < 10^{-4}M$] can coagulate colloidal dispersions of positive surface potential. At higher concentrations of polymeric silica these dispersions become restabilized as negative sols, apparently because of specific adsorption of the anionic polysilicates onto the sol particles. The interaction caused by specific adsorption may outweigh electrostatic repulsion. Under certain conditions anionic polysilicates can flocculate AgBr sols of negative surface potential. Thus, suitably prepared polymeric silicates exhibit properties similar to those of organic polyelectrolytic flocculants.

Polysilicates are adsorbed at solid-solution interfaces and find application as coagulants and coagulation aids. Thirty years ago Baylis (1937) and Graf and Schworm (1937) proposed sodium silicate modified by acidification ("activated silica") as a coagulant aid. Despite an extensive literature on polymerization and aggregation properties of acidified sodium silicate solutions (Iler, 1955; Bechtold, 1955; Stöber, 1957; Baumann, 1959; Debye and Nauman, 1961), little interpretative explanation for the mode of preparation and the mode of action of polysilicates in coagulation has been given. It is the objective of this paper to delineate conditions under which polysilicates are formed and to provide a simple method for evaluating the coagulative properties of polysilicates.

Polysilicates as Polynuclear Hydroxo Complexes

The colloid-chemical properties of polysilicates are similar to those of hydrolyzed metal ions. Multivalent metal ions and metalloids (Si, B, Ge) have a tendency to coordinate with hydroxo and oxo ligands to form multinuclear species, $Me_6(OH)_p^{±z}$. The polyanions of Si, B, and Ge, as well as the hydrolysis systems of Al(III), Fe(III), and Cr(III) and the multinuclear anions of Cr(VI), Mo(VI), and V(V) are representative examples (Sillen, 1959). In solutions that are oversaturated with respect to the usually insoluble hydroxide or hydrous oxide, a sequence of progressive condensation and hydroxylation usually leads to multimeric soluble intermedi-

ates, and to colloidal hydroxo or oxo polymers. Ultimately insoluble polymeric complexes of indefinite size are formed. These latter are usually referred to as the insoluble metal or metalloid hydroxides (or amorphous hydrous oxides) (Stumm, 1967).

Coagulation by multivalent metal ions, as practiced in water treatment, is brought about by metal ion hydrolysis species and not by the free multivalent metal ions (Mattson, 1928; Stumm and Morgan, 1962; Fuerstenau *et al.*, 1965; Matijević and Janauer, 1966). Kinetic intermediates in the transition from mononuclear species to precipitates are efficient coagulants. Matijević and collaborators have shown that multinuclear hydroxo complexes are strongly sorbed on colloidal dispersions and are able to reverse the charge of and restabilize lyophobic colloids.

It is shown here that thermodynamically unstable polysilicates are formed under conditions of oversaturation with respect to amorphous silica and that these polynuclear hydroxo species can be readily detected by coagulation. As shown by Lagerstrom (1959) and Ingri (1959), the mononuclear orthosilicic acid, $Si(OH)_4$, and its conjugate bases, $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$, are in equilibrium with multinuclear species containing a low number (three or four) of Si atoms. The results of these equilibrium studies together with information on the solubility of amorphous silica permit the delineation of the concentration-pH domains for mononuclear silicates, multinuclear stable silicates, and unstable polysilicates (Figure 1).

Solubility of Amorphous SiO_2 and Mononuclear SiO_2

Up to pH values of approximately 9, the solubility of amorphous SiO_2 is constant. It has been reported by various investigators (Alexander *et al.*, 1954; Baumann, 1955; Krauskopf, 1956; Stoeber, 1967) to be 100 to 150 mg. of SiO_2 per liter (1.67 to $2.5 \times 10^{-3}M$) at $25^\circ C.$, the soluble species being in the form of $Si(OH)_4$. This information, together with Lagerstrom's (1959) data on silicate equilibria (Table I), permits computation of the solubility of amorphous SiO_2 for the entire pH range and the relative concentration of the species that are in equilibrium with amorphous SiO_2 . Within neutral and slightly alkaline pH ranges, only $Si(OH)_4$ occurs. Under alkaline conditions, the solubility of SiO_2 becomes enhanced because of the formation of monomeric and multimeric silicates. Although there is some uncertainty concerning the exact nature of the multimeric species, the experimental data of Lagerstrom (1959) and Ingri (1959) leave no doubt on the existence of multinuclear species. Even if multinuclear species other than $Si_4O_6(OH)_6^{2-}$ were present, the solubility characteristics of SiO_2 would not be changed markedly. Amorphous silica is metastable in comparison to quartz. The rate of crystallization of quartz is so slow in the low temperature range that the solubility of

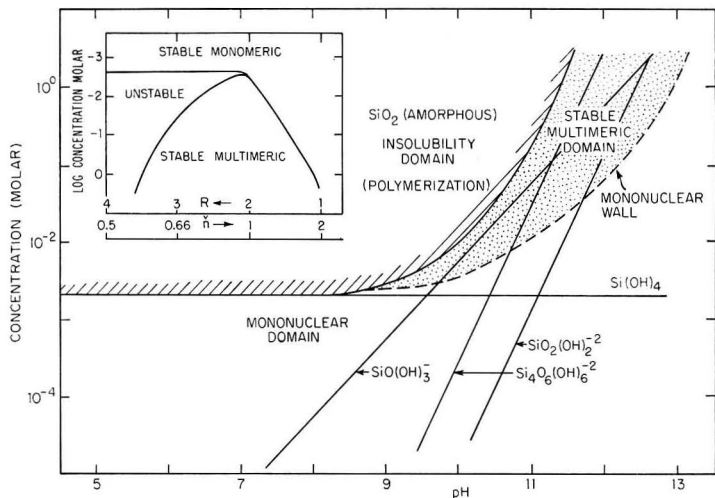


Figure 1. Species in equilibrium with amorphous silica

Diagram computed with equilibrium constants (25° C.) given in Table I. Line surrounding shaded area gives maximum soluble silica. Mononuclear wall represents lower concentration limit below which multinuclear silica species are not stable

Insert. Stability and instability domains as a function of R ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio) or \bar{n} (OH^- bound per SiO_2) and $[\text{Si}_T]$. R (or \bar{n}) remain constant upon dilution of a sample

Table I. Silicate Equilibria

No.	log k (25° C.)
1. $\text{SiO}_2(\text{s}) (\text{amorph}) + 2 \text{H}_2\text{O} = \text{Si}(\text{OH})_4$	-2.7
2. $\text{Si}(\text{OH})_4 = \text{SiO}(\text{OH})_3^- + \text{H}^+$	-9.46
3. $\text{SiO}(\text{OH})_3^- = \text{SiO}_2(\text{OH})_2^{2-} + \text{H}^+$	-12.56
4. $4 \text{Si}(\text{OH})_4 = \text{Si}_4\text{O}_6(\text{OH})_6^{2-} + 2 \text{H}^+ + 4 \text{H}_2\text{O}$	-12.57

Literature data for log k of Reaction 1 vary between -2.5 and -2.85. Data for Reactions 2 to 4 are those given by Lagerstrom (1959) valid for a 0.5M NaClO_4 medium.

amorphous silica represents the upper limit of dissolved aqueous silica (Siever, 1957).

Also indicated in Figure 1 is the "mononuclear" wall—i.e., the concentration of total silica that must be exceeded to encounter multi- or polynuclear species in the solution. The mononuclear wall follows the line characterizing $[\text{Si}(\text{OH})_4]$ up to a pH of approximately 9; the concentration of mononuclear Si then increases with increasing pH. The line has been calculated using the data in Table I for the condition $100 [\text{Si}]^{(\text{multimeric})} = [\text{Si}]^{(\text{monomeric})}$. Distribution diagrams for the various silicate species in the alkaline pH range are given in Figure 2 for three $[\text{Si}_T]$ concentrations. The tendency to form multinuclear species increases with $[\text{Si}_T]$.

Three domains in the concentration-pH diagram are of importance: (1) the insolubility domain—i.e., the range where amorphous SiO_2 precipitates—(2) the multimeric domain where silicon polyanions are stable; and (3) the monomeric domain where mononuclear Si species $[\text{Si}(\text{OH})_4]$, $\text{SiO}(\text{OH})_3^-$, and $\text{SiO}_2(\text{OH})_2^{2-}$ prevail thermodynamically.

Natural waters are in the monomeric range, the dissolved silica being predominantly (below pH 9) present as silicic acid. Commercially available concentrated silicate solutions are in the multimeric domain. In this range silicate glass (produced in the soda ash fusion process) or silicate powders within appropriate ratios of SiO_2 to alkali dissolve when brought into contact with water.

Solutions that are oversaturated with respect to amorphous silica are unstable and a precipitate will eventually be formed.

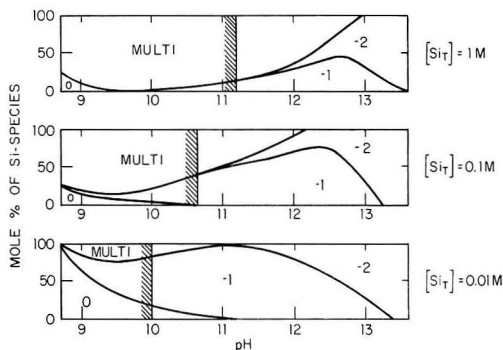


Figure 2. Distribution of Si species as a function of pH

- 0. $\text{Si}(\text{OH})_4$
- 1. $\text{SiO}(\text{OH})_3^-$
- 2. $\text{SiO}_2(\text{OH})_2^{2-}$

Extent of hydroxo complexation depends on pH. At given pH, tendency to form multinuclear species increases with increasing $[\text{Si}_T]$. Shaded boundary indicates pH at which solution becomes oversaturated with respect to amorphous SiO_2 . At a pH value lower than this boundary, polymerization of silicic acid occurs and ultimately amorphous SiO_2 is formed

The precipitation of amorphous silica apparently proceeds in a series of steps:

Mono- or oligonuclear silica species will condense by formation of Si-O-Si bonds to polysilicates (polymerization). Further polymerization accompanied by crosslinking reactions and aggregations (by van der Waal forces) leads to negatively charged silica "sols." Further aggregation may eventually lead to the formation of gels.

This polymerization, aggregation, and gelation reaction can be stopped and slowly reversed if the solution is brought outside the insolubility range. Dilute polymeric silicates may be prepared by bringing soluble silicates into the insolubility range—for example, by acidifying a sodium silicate solution of appropriate concentration. In the insolubility domain, silicates polymerize; subsequent dilution gives solutions containing polysilicates or colloidal SiO_2 aggregates which, de-

pending on the detailed history or preparation, remain "active" as coagulants for long periods of time (hours to weeks).

Average Number of Hydroxides Bound per SiO₂. The concept that silicate solutions become unstable and polymerize whenever their concentration-pH range is within the insolubility range has been suggested by Alexander (1953), Baumann (1959), and Lagerstrom (1959). It makes it easier to understand and generalize many observations and provides a unifying guideline for the preparation of polysilicates and for their practical application. Some of these generalizations can be better appreciated if an additional parameter is introduced that was helpful in characterizing silicate solutions and in defining the boundary between the stable multimeric domain and the unstable insolubility (polymerization) range. This parameter is the ligand number \bar{n} , sometimes also called the formation function; it measures the average number of moles of OH bound n_{OH^-} per mole of SiO₂, n_{SiO_2} . $\bar{n} = n_{OH^-} / n_{SiO_2}$. \bar{n} can be calculated from the electroneutrality condition—i.e., from the difference of total added base (such as NaOH) and the equilibrium OH⁻ and H⁺ concentration. For example, in any mixture of SiO₂ and NaOH, the electroneutrality condition is given by

$$[Na^+] + [H^+] - [OH^-] = [SiO(OH)_3^-] + 2[SiO_2(OH)_2^-] + 2[Si_2O_7(OH)_6^{2-}] \quad (1)$$

The right-hand side of Equation 1 represents the number of OH⁻ ions bound in excess of Si(OH)₄. Thus \bar{n} can be calculated:

$$\bar{n} = \frac{[Na^+]}{[Si_T]} + \frac{[H^+] - [OH^-]}{[Si_T]} = \frac{n_{OH^-}}{[Si_T]} \quad (2)$$

As shown by Lagerstrom, \bar{n} is related to the molar ratio of SiO₂ to Na₂O, R . Because of almost equal formula weights of SiO₂ and Na₂O, the ratio in grams is practically the same. The first term in Equation 2 can be replaced by $2/R$, and since the second term is usually negligible, we have

$$\bar{n} \cong 2/R \quad (3)$$

The function \bar{n} , or the ratio R , is a convenient parameter because neither varies with the dilution for a given silicate solution. With the help of the equilibrium constants given in Table I and using Equations 2 to 4, \bar{n} and R have been computed for the boundaries between the insolubility range and the soluble multimeric domain and between the latter and the mononuclear solubility range (insert, Figure 1). All commercial soluble silicate solutions (water glass), in the soluble multimeric domain, in accord with the boundary given in this figure, have R values smaller than 4. Typical commercial products have ratios between 2.2 and 3.5. One product with $R = 3.75$ is available. On the more alkaline side (larger \bar{n} , smaller R) solutions of sodium orthosilicate (Na₂SiO₄, $R = 0.5$, $\bar{n} = 4$) and sodium metasilicate (Na₂SiO₃, $R = 1$, $n = 2$) contain at all concentrations exclusively mononuclear species. Nauman and Debye (1951), using light scattering, calculated molecular weights of about 70 (indicative of monomers) for silicate solutions with $R \leq 1$, while multinuclear species having molecular weights of a few hundred were found in the range $1 < R < 3.75$. The insert in Figure 1 also illustrates that the dilution of silicate solutions with R values between about 2.75 and 3.75 ($\bar{n} = 0.53$ to 0.73) leads to un-

stable polymeric species, while mononuclear silica solutions are obtained by dilution of solutions with $R < 2$ ($\bar{n} > 1$).

Materials and Methods

Particles of aluminum oxide with a diameter between 0.01 and 0.04 micron and a surface area of approximately 60 sq. meters per gram were obtained from Particle Information Service, Los Altos, Calif. Ludox (E. I. du Pont de Nemours & Co.) was used as amorphous silica with particle diameters of approximately 15 μ (Ludox LS) and 7 μ (Ludox SM), respectively. Electrophoretic measurements were made using a Briggs cell.

Polysilicic acid solutions were prepared by neutralizing sodium silicate solutions (usually sodium metasilicate, Na₂SiO₃·9H₂O) with nitric acid or by passing through a Dowex 50W-X8 cation exchange resin in the H⁺-form. Where buffering was necessary, small quantities of HCO₃⁻ (<10⁻³M) and CO₂ were added. A sketch with some figures indicates the history of preparation of the polysilicic acid solution—for example, in Figure 4, curve 1 was obtained by neutralizing a 5 × 10⁻²M sodium metasilicate solution to pH 6 and keeping it at this pH for 30 minutes (polymerization time, $t_p = 30$ minutes) before quenching by diluting it to 10⁻³M. Polymeric solutions can be stabilized for periods of up to 2 weeks by acidifying them to pH 2.5 (curve 4, Figure 4).

The flocculation of silver bromide *in statu nascendi* was carried out as follows: An appropriate volume of the polysilicic acid solution (usually 10⁻³M) was mixed with 10 ml. of a 2 × 10⁻²M AgNO₃ solution and diluted with distilled water to 50 ml. Then 50 ml. of a 10⁻³M KBr solution were added to the Ag⁺ solution. Such solutions contain 2 × 10⁻³M Ag⁺ and 5 × 10⁻⁴M Br⁻ and contain, in the absence of polysilicate, positively charged AgBr sols. AgBr sols with an incipiently negative surface potential were prepared by adding a solution containing AgNO₃ and polysilicic acid to a solution of KBr, the final solution containing 5 × 10⁻⁴M Ag⁺ and 2 × 10⁻³M Br⁻. Blanks were run with solutions containing equivalent concentrations of AgNO₃ but no KBr, in order to ascertain that within the pH and concentration range investigated no precipitation between Ag⁺ and silicate or polysilicate occurs.

Turbidity was estimated by measuring the scattering intensity (the ratio of the light scattered at 90° to the light transmitted) with a Brice-Phoenix light-scattering photometer using a wavelength of 546 μ and square cells with a light path of 2.5 cm. In the experiments with Al₂O₃ the extent of flocculation was estimated by measuring the turbidity of the supernatant after a 1-hour settling period. With the AgBr sols, however, the turbidity of the suspension was measured. Correspondingly, in these experiments coagulation is accompanied by an increase in the intensity of the scattered light. Scattering intensity was measured 60 minutes after mixing of the solutions. To investigate effect of surface area of the sol upon the destabilization curve, concentration of Al₂O₃ and, correspondingly, the surface area was varied within a 10-fold range.

All experiments were carried out under thermostatic conditions at 25° C.

Coagulation and Restabilization

The effect of silicates on the stability of a colloidal Al₂O₃ dispersion is illustrated in Figure 3. Monomeric orthosilicic acid, prepared by acidifying (with HNO₃) dilute sodium

metasilicate solutions ($[Si_T] < 10^{-2.7}M$), does not influence the stability of the positively charged Al_2O_3 sol and does not affect the electrophoretic mobility of the Al_2O_3 particles (curve 2). On the other hand, dilute polysilicic acid solutions, prepared by first acidifying and subsequently diluting $2 \times 10^{-2}M$ sodium metasilicate solutions, can coagulate colloidal Al_2O_3 dispersions (curve 1). Destabilization is observed at silica concentrations of $[Si_T] \geq 10^{-6}M$ (0.06 mg. of SiO_2 per liter). At higher silica concentrations ($[Si_T] > 10^{-4.4}M$) the Al_2O_3 sols become redispersed. Figure 3 shows that destabilization is accompanied by a decrease in electrophoretic mobility—i.e., a reduction of the effective surface potential. At $[Si_T] \approx 10^{-4.4}M$ this potential is reduced to zero; at higher concentrations the charge on the Al_2O_3 is reversed and the Al_2O_3 dispersion becomes restabilized as a negative sol. Destabilization and restabilization of the sol are caused by specific adsorption of the anionic polysilicates on the Al_2O_3 particles. That the change in colloid stability is due to adsorbed polymeric silica is also evident from the linear relationship observed between the concentration of polysilicate necessary for optimum destabilization—i. e., $[Si_T]$ at the minimum of the coagulation curve—and the aluminum oxide concentration, or more precisely the surface area concentration (insert, Figure 3).

Destabilization of AgBr Sols. Coagulation effects of polysilicates on positively charged silver bromide sols *in statu nascendi* are shown in Figures 4 to 6. Again, polysilicates at very dilute concentration destabilize and at slightly higher concentrations restabilize these sols, while orthosilicic acid does not affect their stability (Figure 4).

The results depicted in Figure 4 are representative of a

large number of experimental runs. In all cases, coagulation of positive AgBr sols was observed only if the silica solution was introduced into the pH-concentration range of the insolubility domain. Simple dilution of a low ratio sodium silicate ($R < 2$) results in a coagulation-inactive solution of orthosilicic acid. Solutions prepared by diluting high ratio silicates ($R > 2$) are active and contain polysilicic acid. Obviously, coagulation of silver halogenide sols is a convenient and very sensitive method of determining whether silicate solutions contain multinuclear or mononuclear silica species. Furthermore, the coagulation method can be used to evaluate operationally the various parameters that influence the activity of polysilicates. The coagulative properties of polysilicates prepared by neutralizing solutions of sodium metasilicate do not depend upon the neutralizing agent: No difference was observed in the activity of polysilicates if neutralization was made with a mineral acid or with the aid of an ion exchanger. However, solutions prepared by neutralizing high ratio silicates ($R = 3.3$) substantially increased the scattering intensity at the coagulation maximum without changing the silica concentration necessary to produce the coagulation (Figure 4b).

Effect of pH and Neutral Electrolytes. The activity of polysilicates in destabilizing AgBr sols is influenced by pH and by the presence of neutral electrolytes. Upon addition of $NaNO_3$ ($10^{-2}M$) and Na_2SO_4 ($10^{-4}M$), the scattering intensity at the coagulation maximum increases and the silica concentration necessary to produce coagulation decreases (Figure 5). The salt concentrations used are below those required to coagulate AgBr sols in the absence of polysilicates. Figure 6

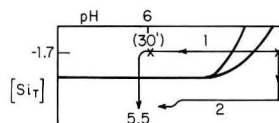
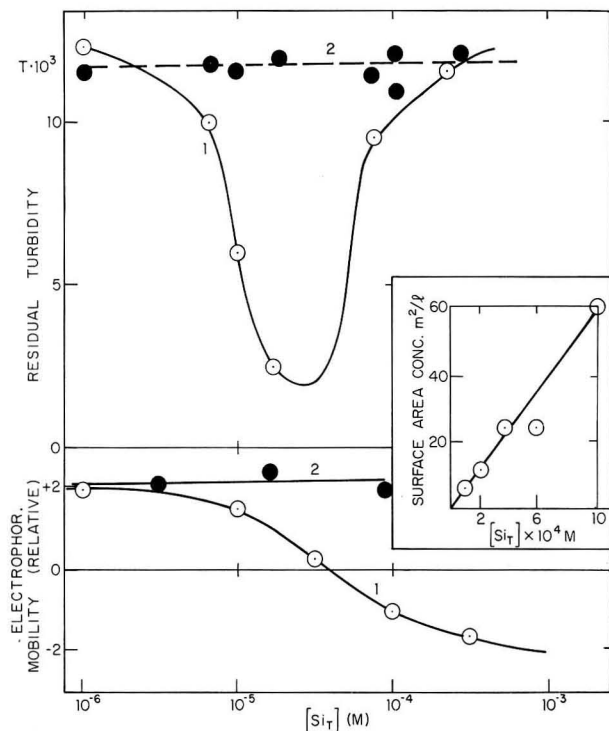


Figure 3. Coagulation and restabilization of Al_2O_3 with polysilicate (pH = 5)

Turbidity (scattering intensity) of supernatant after 1-hour settling and electrophoretic mobility as a function of $[Si_T]$

1. Polysilicate 2. Orthosilicic acid. Orthosilicic acid $Si(OH)_4$ at concentrations comparable to polysilicic acid has no effect on surface potential and stability of Al_2O_3 suspension. A sketch (describing stability relations as in Figure 1) describes mode of preparation of polysilicate

Insert. "Stoichiometric" relation between polysilicate concentration necessary to destabilize Al_2O_3 and surface area concentration of Al_2O_3

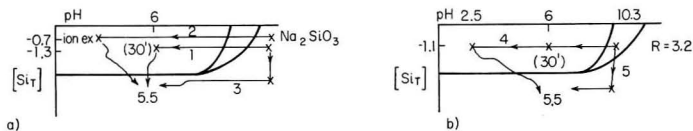
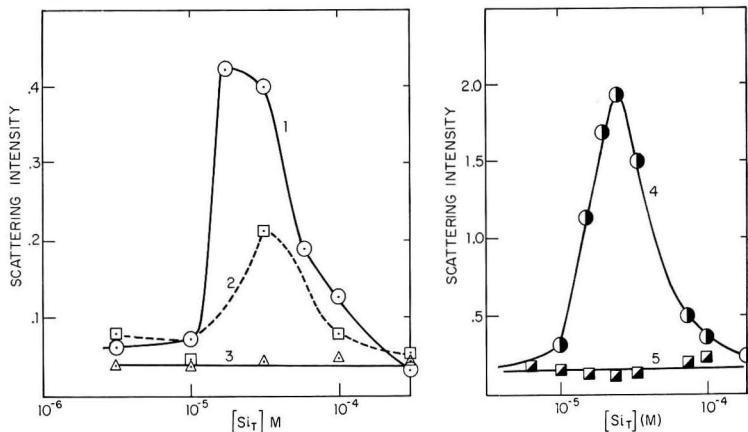


Figure 4. Coagulation and restabilization of positively charged AgBr sols by polysilicate

a. Polysilicates prepared by neutralizing with HNO_3 (1 and 3) or with ion exchange (2) solutions of sodium metasilicate. *b.* Commercially available multimeric silicate with a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of $R = 3.2$ neutralized with HNO_3



illustrates the effect of pH upon scattering intensity and optimum coagulation concentration.

Polymerization pH and Polymerization Time. Additional pertinent variables affecting the coagulating behavior of polysilicates are the polymerization pH (pH to which sodium silicate solution was neutralized); polymerization concentration, C_p ; polymerization time, t_p ; and age of dilute polysilicate solution, t_a . In accord with observations made by many others (Iler, 1955; Bechtold, 1955; Baumann, 1959) the rate of polymerization to "active" polysilicates is strongly pH-dependent and is influenced by C_p . It is very fast in neutral and slightly alkaline solutions and extremely slow at low pH values (pH 2 to 3).

In the neutral and slightly alkaline pH region solutions with $10^{-1}M \geq C_p \geq 10^{-2}M$ polymerize so fast that their coagulation activity toward AgBr sols after dilution remains unchanged after a polymerization time of 30 minutes (Figure 6b). In the acid pH range, polymerization is so slow that the coagulative properties of incipiently polymerized solutions remain unchanged for days if after polymerization the pH is adjusted to 2.5. This slow polymerization at low pH can be used conveniently to stabilize polysilicic acid solutions for periods of up to 2 weeks.

Aging of Dilute Polysilicate Solutions. Dilute polysilicate solutions ($[\text{Si}_T] \geq 10^{-2.7}$) are undersaturated with respect to amorphous silica (mononuclear domain) and will depolymerize to orthosilicic acid; $10^{-3}M$ solutions (pH 5 to 6) maintain the coagulation behavior characteristics of polysilicates for long periods (Figure 6a). After aging for approximately 20 days, however, a destabilization of AgBr sols can no longer be observed; apparently after this period depolymerization to $\text{Si}(\text{OH})_4$ has become complete.

Polysilicic Acid and Colloidal Silica. The experimental results described here do not permit a clear distinction as to whether our solutions contain polymerized silicic acids of high molecular weight and colloidal dimension or discrete particles of amorphous SiO_2 of colloidal size. Figure 7, however, shows that our polysilicate solutions are able to destabilize

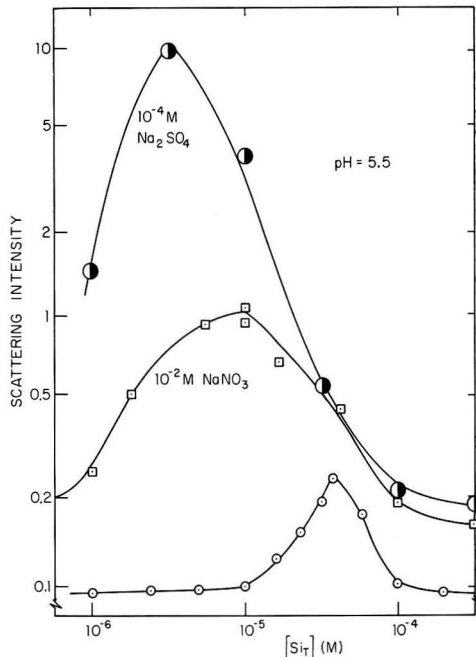


Figure 5. Coagulation of positive AgBr sols in presence of polysilicate and counter ions

Polysilicate prepared as in curve 1 of Figure 3

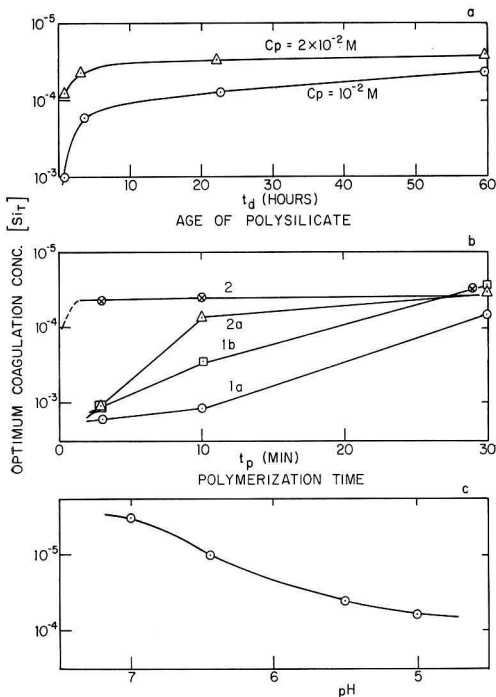
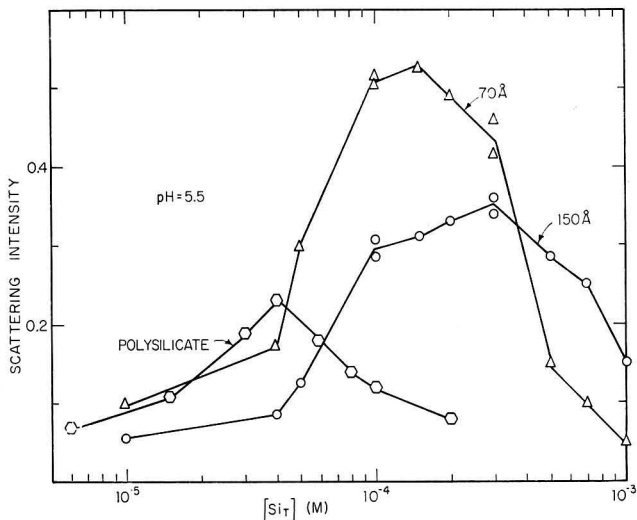


Figure 6. Variables affecting the activity of polysilicates
a. pH = 5.5, $t_p = 30$ min. *b.* pH = 5.5, $t_d > 60$ min. For 1a and 2a, $10^{-1}M$ and $5 \times 10^{-2}M$ sodium metasilicate neutralized with ion exchanger, respectively. For 1 and 2, $5 \times 10^{-2}M$ and $2.10^{-1}M$ sodium metasilicate neutralized with HNO_3 , respectively. *c.* Polysilicates prepared as given by curve 1, Figure 3

Figure 7. Comparison of polysilicate with discrete amorphous SiO_2 particles
 Polysilicates prepared as in curve 1 of Figure 3



AgBr sols at Si_T concentrations much lower than solutions of discrete particles of SiO_2 of 150 and 70 Å, respectively.

Interaction of Polysilicic Acid with Negatively Charged Silver Bromide. Figure 8 gives a flocculation curve describing the destabilization of negatively charged AgBr sol *in statu nascendi* by anionic polysilicic solutions. The scattering intensity maximum observed is indicative of destabilization of the AgBr sol. The addition of polysilicate does not affect the zeta potential of the AgBr sols (Figure 8). Destabilization of negatively charged AgBr is only observed in solutions of pH < 6.

Discussion

The coagulation method can be used to investigate the polymerization of silicic acid and to evaluate the conditions under which polysilicates are formed. The results reported confirm that silicate solutions undergo polymerization if they are introduced into the (Si_T) -pH domain of oversaturation with respect to amorphous silica. Polymerization can be quenched and slowly reversed if the solutions are brought outside the insolubility range by dilution or pH adjustment.

Specific Adsorption. With positively charged Al_2O_3 and AgBr sols, the change in colloid stability appears to be caused primarily by specific adsorption of polysilicates from dilute solutions onto the colloidal particles. This adsorption leads to a reversal of charge and a restabilization of the sols. Destabilization is dependent upon the sol concentration or more specifically on the surface area of the dispersed phase. The insert in Figure 3 illustrates that $[Si_T]$ necessary for coagulation increases linearly with the concentration of surface in the dispersion. Such a linear dependence on surface area is not in disagreement with that predicted by a Langmuir adsorption model. A similar linear dependence has been observed for the coagulation of silica by hydrolyzed Fe(III) (O'Melia and Stumm, 1967). Optimum destabilization is observed at a given fractional coverage of the colloid particle surface with polysilicate. When most of the polysilicate added to the solution is adsorbed ($[Si_T] \approx [Si_{ads}]$), the Langmuir equation reduces to

$$[Si_T] = \Gamma_M S \theta \quad (4)$$

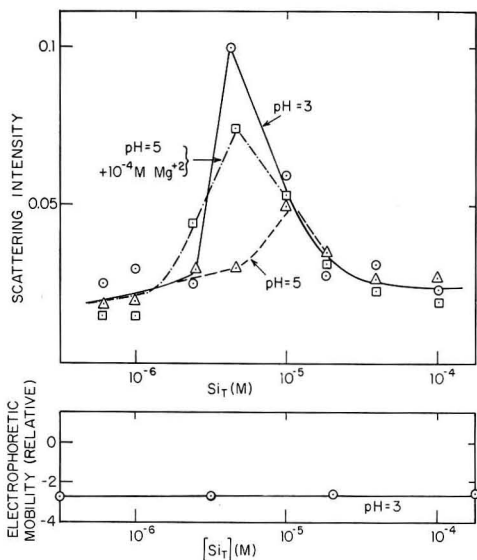


Figure 8. Flocculation of negative AgBr sols by anionic polysilicate
Polysilicates prepared as in curve 1, Figure 3

where Γ_M , S , and θ are the sorption capacity (moles of Si per square meter), the surface area of the sol in the dispersion (square meters per liter), and the fraction of surface covered, respectively. Thus, under these conditions, $[Si_T]$ required to produce a given surface coverage and in turn to destabilize the dispersion is directly proportional to the concentration of surface in the dispersion.

Adsorption and Double Layer Interaction. The energy of adsorption of polysilicates onto the sol particles cannot be neglected in considering the total energy of the double layer interaction. Very little is known about the short range chemical interaction forces involved in lowering the effective surface potential by adsorption of polymers. Naumann and Dresler (1966), in experiments on coagulation of chrysotile asbestos suspensions, have recently shown a definite correlation between critical coagulation concentration and ion volume of the coagulants. The destabilization characteristics of polysilicates are comparable to those observed with solutions of polynuclear hydroxo metal species and polyelectrolytes. These solutions, too, will restabilize sols at sufficiently high concentrations because of adsorption of the destabilizer species onto the colloidal particles.

That the energy of interaction due to sorption may outweigh purely electrostatic effects is evident from the observation (Figure 8) that AgBr sols of negative surface potential can be flocculated by anionic polysilicates. In such aggregates particles are bridged together by polymeric silicates. A similar mechanism has been postulated for the flocculation of negative sols by anionic polyelectrolytes (Ruehrwein and Ward, 1952; La Mer and Healy, 1963). Nevertheless, effects due to electrostatic interaction are also recognizable: The flocculation between polysilicates and negatively charged AgBr particles is enhanced by decreasing the pH of the solution or by adding multivalent cations, thus decreasing the electrostatic repulsive forces. Similarly, destabilization of positively charged AgBr by polymeric

silicates is aided by adding counter ions and by raising the pH (Figures 5 and 6). With increasing counter ion concentration and charge, less polysilicate is necessary to produce coagulation.

Conclusions

It is not within the scope of this study to draw conclusions as to the type of polymers, the structural arrangement, or the size or molecular weight of the polysilicates. Many observations, including preliminary molecular weight determinations, not reported here, suggest that the polysilicates used in this investigation are of rather high molecular weight (10^4 to 10^6 g), but it remains uncertain whether the solutions contain soluble, internally hydrated, polymeric silicic acids of colloidal dimensions or discrete particles of colloidal size. Obviously, however, the polysilicates are more active in destabilizing sols than the commercially available dense colloidal silica particles (Figure 6). While the "activity" of polymerized silicic acid as a coagulant depends on the detailed history of its preparation, our observations show that polymeric species performing in a uniform manner can be reproduced and that the coagulation method is well suited to determine some of the pertinent operational surface chemical characteristics of the preparations. The solubility of amorphous silica represents the upper limit of dissolved stable aqueous silica.

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The Surface Chemistry of Active Carbon

A Discussion of Structure and Surface Functional Groups

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■ Active carbon is an effective adsorbent for removal of dissolved organic substances from waters and wastewaters. The physicochemical nature of the surface of carbon is an important factor in the adsorption process, and should be considered in selection or preparation of carbons for specific applications. The principal objective of the present discussion is the review of current information on this subject and development of an elementary conceptual model for description of the active carbon surface. The purpose of this model is to delineate some of the more significant factors to be considered in interpretation of sorption phenomena associated with active carbon, and to provide a basis for further research in this area. Considerations of importance in this model are parameters which influence both the structure and the surface chemistry of the active carbon. There is strong indication of the need for continuing research on the definition of the nature of surface functional groups, and on the particular conditions of preparation which will produce an active carbon best suited for a specific application.

Exacting demands are being made upon existing water resources to meet the requirements of a highly industrialized society. These demands can be expected to mount in the future, for continuing population expansion and technological development lead naturally to both more extensive and more intensive use of available supplies of water, and ultimately to the pollution and degradation of the quality of these waters. Much of the water currently available to a large segment of society has been subjected to previous use. Indeed, multiple reuse of water is not uncommon today; planned and deliberate reuse is expected to be an even more significant factor in water resources management in the years ahead. Evidently, as reuse practice increases, more stringent requirements will be placed on the treatment of waters and wastewaters, and more effective removal of persistent materials, which might otherwise build up to intolerable concentrations during several reuse cycles, will be required.

Adsorption on active carbon has emerged as a particularly attractive method for removal of perdurable organic pollutants from waters and wastewaters. Although active carbon has been widely employed for the past three or four decades for removal of taste- and odor-producing materials from water supplies, its use in this application has been largely occasional

and for the most part quite inefficient. While it has been possible to tolerate such inefficiencies in an application involving relatively low concentrations of pollutants, extensive treatment of wastewater for direct reuse will require that this process be developed to a high degree of effectiveness and efficiency for obvious technological and economic reasons.

In order that engineers responsible for the design of active carbon facilities for water or waste treatment be in position to articulate specifications for maximum efficiency of use in particular situations, they must have at their disposal precise information about the nature and behavior of active carbon and about the adsorption process. Much recent research has centered on the development of such information for this purpose (Johnson *et al.*, 1964; Joyce and Sukenik, 1964; Weber, 1966; Weber and Morris, 1963 and 1964), but there is yet more to be learned and set forth regarding the properties and surface chemistry of active carbon and about factors which affect its behavior as an adsorbent. Active carbon is effective for removal of organic substances of relatively low solubility in water primarily because it provides a large interfacial area at which such substances may accumulate. However, any interpretation of the adsorptive behavior of active carbon based solely on the extensiveness of the surface of this material is obviously incomplete, for equal weights of two carbons prepared from different raw materials and/or by different methods may possess the same total surface area yet function differently as adsorbents. Part of such differences in adsorptive behavior can be explained in terms of relative pore size distributions, but part must also be attributed to differences between the respective surface properties of the carbons. The surface of any active carbon is comprised in part of residual electron- and ion-exchange functional groups, connected by electron-conducting bond systems (Garten and Weiss, 1957*b*). The nature of these functional groups is determined to a large extent by the method of activation as well as by the type of raw material from which the carbon is prepared. With the existence of electron- and ion-exchange groups at the surface of carbon, it is reasonable to expect that electrolytes in solution may interact with the carbon to influence its behavior as an adsorbent. Indeed, such interactions could markedly affect the over-all adsorption process under certain conditions, possibly effecting changes in the process which may be put to good advantage to achieve higher efficiency or enhanced effectiveness of removal of pollutants. Weber and Morris (1964), for example, have shown that the hydrogen ion activity of a solution affects both rate and capacity for adsorp-

tion of negatively charged species of sulfonated alkylbenzene from aqueous solution by carbon. These authors have interpreted their results as indicating that decreasing pH leads to an increasing association of the positively charged hydrated proton with negatively charged functional groups on the active carbon surface, thus neutralizing electrostatic repulsive forces to allow the charged organic species more easily to migrate through the pore spaces and be adsorbed at inner surface sites. Garten and Weiss (1957b) have interpreted changes in hydrogen ion activity observed upon addition of active carbon to acidic or basic solutions in terms of an interaction between the acid or base and a basic or acidic heterocyclic surface structure, respectively. This interaction is currently being studied in detail in the authors' laboratories to determine more precisely its effect on the sorptive properties of active carbon.

Other inorganic species also seem to be important in their effects on the manner in which active carbon functions in aqueous solution as a sorbent for organic substances. Joyce and Sukenik (1964) have observed a 50% increase in ash content (from 6 to 9% and from 12 to 18%) to be accompanied by a 50% decrease in the capacity of an active carbon after 10 cycles of sorption from a solution of the calcium salt of a sulfonated alkylbenzene followed by thermal regeneration. Because the ash was soluble in acid solution, but insoluble in near neutral solution, these authors suggest that acid treatment in conjunction with thermal regeneration may prove feasible as a means for restoring active carbon to near original capacity. Before such treatment is effected however, one should know how the acid may affect the active carbon surface, and, therefore, how it may influence the adsorption process.

Various chemical oxidizing agents can also interact with active carbon in aqueous solution to increase the amount of chemisorbed oxygen at the carbon surface (Puri *et al.*, 1961). Once more, however, the effect of the presence of this oxygen on the sorptive properties of active carbon has not yet been sufficiently defined.

Apparently, then, much more information is needed regarding the nature of interactions which occur between the various functional surface groups of active carbon and electrolytes in aqueous solution, with particular reference to the effects of such interactions on the sorptive properties of the carbon. The present discussion has as its objective the examination of such information as is currently available concerning the structure and nature of active carbon, and the presentation of a relatively unified concept or model for description of the surface chemistry of this material. This model, hopefully, will provide a reasonable basis for further research directed to the delineation of the surface properties of carbon significant in its applications for water and wastewater treatment.

Preparation of Active Carbon

The term active carbon actually implies a rather broad family of substances, with individual species being characterized by sorptive and catalytic properties rather than by definite structure or specific chemical composition (Hassler, 1963). Particular properties may be imparted to an active carbon either by starting with different raw materials or by utilizing different preparative procedures.

Substances from which active carbons are manufactured are carbonaceous in nature, usually carbohydrates; wood, coal, sugar, nut shells, and vegetable matter are examples of typical raw materials. Differences in active carbons may obtain as a result of the particular characteristics of the starting material, but many of the differences commonly ascribed to dissimilar starting materials may be due in fact to noncarbonaceous impurities. In addition, preparative conditions may be varied and selected additives employed to produce a particular active carbon of desired structure and surface properties.

The production of active carbon involves first the formation of a char from the raw material. The starting material is heated—usually in the absence of air—to a temperature sufficient to effect drying and to drive off volatile fractions. Carbonization is then accomplished by elevating the temperature, producing a carbonaceous char (Johnson *et al.*, 1964; Hassler, 1963). In this process the temperature is increased slowly to allow time for each step to be completed before the next begins. The entire process is usually carried out below 600° C., although exceptions do exist. Additives such as calcium chloride, magnesium chloride, zinc chloride, or any one of a number of similar materials may be used to catalyze the process and to impart certain characteristic properties to the finished product (Hassler, 1963).

The char developed in the carbonization process has relatively little internal surface area, and because a large surface is required for most adsorption applications, the char is generally "activated" by treatment with oxidizing gases under carefully controlled conditions. The oxidizing gases—commonly carbon dioxide, steam, and air—attack the more readily oxidizable portions of the char, resulting in the development of a porous structure and an extensive internal surface. The temperature of activation is a critical factor in the process, as will be discussed in more detail shortly. Treatment of the char with reagents such as chlorine, dolomite sulfates, and several other substances to develop special properties in the finished product and to catalyze the action of the oxidizing gas is often effected prior to the activation process (Hassler, 1963). According to Johnson *et al.* (1964), carbonization and activation can sometimes be carried out in one step, rather than as separate operations. The total surface area of a carbon, by far the greatest percentage of which is internal, can be as great as 2,500 square meters per gram after activation.

Structure and Structural Development

The molecular and crystalline structure of active carbon is an important determinant of the types of functional groups which can exist on the surface and is, therefore, an important consideration in any discussion of the surface chemistry of this material. Although there is little direct information available on the structure of active carbon, much can be derived from existing data on the structure of carbon black. Very little chemical difference exists between these two substances, and the only apparent physical difference is that the carbon black has much less internal surface area (Garten and Weiss, 1957b).

As a basis for discussion of the active carbon structure, it is appropriate to consider first the structure of ideal graphite in that it is closely approximated in the basic structural unit of both active carbon and carbon black (Wolff, 1959; Heckman, 1964; Walker, 1962).

The structure of ideal graphite is given in Figure 1. According to Walker (1962), this structure is composed of a system of infinite layers of fused hexagons. Within each layer the carbon-carbon bond distance is 1.415 Å, indicating one-third double bond character. Three of the carbon's four electrons are engaged in forming regular covalent bonds with neighboring atoms and are localized, while the fourth resonates between several valence-bond structures, giving each carbon-carbon bond a one-third double bond character. Relatively weak van der Waals forces act between the parallel layers to hold the distance of separation to approximately 3.35 Å. The carbon layers form an *a-b-a-b-a-b* stacking sequence in which one-half of the carbon atoms in any one plane lie above the center of the hexagons in the layer immediately below it. The carbon atoms are directly superimposed in alternate layers. X-ray diffraction spectra obtained for most natural graphites indicate that this structural configuration is in fact predominant (Walker, 1962).

During the carbonization of the raw material in the preparation of active carbon, small aromatic nuclei, interpreted from x-ray spectrographs as microcrystallites consisting of fused hexagonal rings of carbon atoms having a structure similar to that of graphite, are formed (Wolff, 1959; Heckman, 1964). The diameter of the planes making up the microcrystallite has been estimated as 20 to 50 Å. (Wolff, 1959). The height of stacking is also in the range of 20 to 50 Å., indicating that each microcrystallite consists of 5 to 15 layers of aromatic planes.

Although the structure of the microcrystallite is similar to that of graphite, it differs in many ways. During the formation of the microcrystallite, impurities should be expelled from its interior. However, Walker (1962) states that interior vacancies exist in the microcrystallite and that their formation depends on the method of preparation. Possibly these vacancies contain some of the impurities; the presence of impurities may, in fact, influence the formation of such a vacancy. In addition, the ringed structures at the edges of the planes making up the microcrystallite are often heterocyclic owing to the nature of either the starting material or of the preparation process used (Garten and Weiss, 1957b). Heterocyclic groups would tend to affect both the distance of separation of adjacent planes and the sorptive properties of the carbon. Also, orientation between adjacent planes in the microcrystallite varies from that found in ideal graphitic structure to that of complete random orientation found in turbostratic carbons (Walker, 1962). The definite *a-b-a-b-a-b* stacking order, therefore, does not exist in most active carbons. Functional groups terminating the microcrystallite planes interconnect the microcrystallites, and are at least partially responsible for the turbostratic character in that they prevent orientation of the planes with respect to each other. Because of its special properties and the many differences between it and graphite, Garten and Weiss (1957b) have chosen to compare active carbon with a complex organic polymer rather than with a graphitic type particle.

The structure of the char particle is developed further by

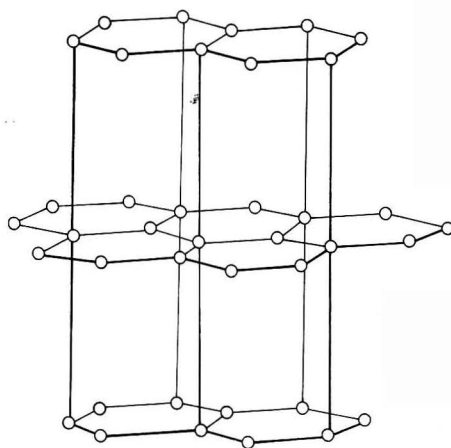


Figure 1. The arrangement of carbon atoms in the graphite crystal (Walker, 1962)

treatment with oxidizing gases at high temperature during the activation process. Dubinin *et al.* (1964), noticed two stages of oxidation in the activation of carbonized sucrose. First, macropores were formed by the burnout of the most reactive material, consisting principally of hydrocarbon radicals attached to the edge carbons of the microcrystallite. Second, micropores were formed mainly by the burnout of microcrystallite planes. The diameter of the micropore is generally on the order of 4 to 10 Å., while the macropore diameter is usually much larger (Wolff, 1958). The majority of internal surface area is contributed by the walls of the micropore. Snow *et al.* (1959), reported that higher ash content causes faster pore development during activation. Inorganic matter appears to cause stress localizations on the surface of the microcrystallite at which points oxidation is initiated much more easily. Once a plane is attacked by an oxidizing gas, oxidation of that plane continues in preference to another area until a stable structure is developed (Wolff, 1959).

Carbonization and activation temperatures are significant considerations in the structural development of active carbons. Riley (Garten and Weiss, 1955) has demonstrated that the size of the microcrystallites of carbons prepared from carbohydrates increases with increasing temperature of carbonization. In addition, the mechanical strength and electrical conductivity of a carbon increase when prepared at temperatures above 700° C. The temperature at which activation is effected is important also because carbonization continues during this process via the mechanisms of actual removal, cracking, or cyclization of functional groups present at the edges of the microcrystallite (Wolff, 1959).

Chemical Nature of the Active Carbon Surface

If we proceed on the basis of the structure outlined above, and neglect for the moment the effects of noncarbonaceous impurities, two major types of surfaces can be postulated for active carbon: the planar surfaces of the microcrystallites and the edges of the carbon planes making up the sides of the microcrystallite.

The planar surfaces are probably relatively uniform in

nature. No attached functional groups should be present because the electrons of the carbon atoms are involved in covalent bonding with neighboring carbon atoms. Because oxidation occurs much more readily at the edge of the carbon plane than on the surface of the plane (Hennig, 1962), few vacancies owing to oxidation during the activation process are expected in the surface plane. The majority of the sorptive processes occurring on this surface would be due then to the relatively weak van der Waals forces, although electrons are available for π -bonding if the sorbate is capable of entering into such a bond (Gasser and Kipling, 1960). Because most of the surface area of a carbon particle is found in the micropores, and because micropores are formed by the "eating out" of microcrystallite planes (Wolff, 1959), the larger percentage of the total surface area is probably of the planar surface type.

The sides of the microcrystallites are more heterogeneous than the planar surfaces, and are characterized by various types of functional groups and vacancies owing to the action of oxidizing gases. Corners or raised positions on the surface have the greatest tendency to participate in the electron-sharing reactions which characterize chemisorption (Zettlemoyer, 1959). Sorption in depressions is probably physical in nature, but the bonds formed in this case should be much stronger than the bonds formed in physical sorption on the planar surface of the microcrystallite.

Although surfaces of the preceding types can be expected for a very pure active carbon, many carbons have large percentages of oxygen, hydrogen, and inorganic ash. The concept of the type of surface available for sorption must be modified somewhat when such substances are present. The presence of hydrogen on the surface of active carbon, for example, lends quite definite properties to that surface. Certain sorption reactions are known to be more or less specific for surfaces comprised of hydrogen sites. Kipling and Shooter (1966) reported that iodine vapor adsorption on Spheron 6 can be interpreted in terms of adsorption, on that part of the surface covered with hydrogen sites, to the exclusion of those portions of the surface covered with oxygen-containing functional groups. Hydrogen presumably exists either in the form of terminal groups on the fused aromatic planes of the microcrystallite or as part of the hydrocarbon functional groups attached to these planes (Wolff, 1959). Wolff (1958) reported that hydrogen is present in amounts ranging from eight to 19 times that of oxygen, on a molar basis, for carbons containing 0.94 to 2.25% oxygen by weight.

Inorganic matter is present in most commercial active carbons to a very significant extent, and its presence has many noticeable effects (Hassler, 1963; Wolff, 1958). The total amount present consists of inorganic constituents originally present in the starting material and various inorganic salts added to catalyze the carbonization and activation processes or to impart special sorptive properties such as selectivity to the active carbon. The fact that strong acid will remove almost all of the ash content of active carbon suggests that the inorganic matter exists primarily on the microcrystallite

surfaces (Wolff, 1958; Blackburn and Kipling, 1955). The special properties which the inorganic salts develop possibly are due to their effect on the active carbon surface and to their interactions with the sorbate or other solution constituents. Sorption on a surface covered with tightly held inorganic species would very likely differ in nature from sorption on an active carbon surface free of such species. Pore structure would also be affected differently by different types of salts used to catalyze the activation process. Possible interactions between the inorganic salts on the active carbon surface and the sorbate or other solution constituents include complex formation, ion-pair formation, precipitation reactions, and oxidation-reduction reactions. Basic studies of the sorptive properties of active carbon should include a careful study of the effect of the active carbon's inorganic constituents.

Electron spin resonance studies of active carbon have suggested free radical structures or structures with unpaired electrons in the microcrystallite (Harker *et al.*, 1961). According to Ingram (1959), large numbers of unpaired electrons are trapped during the carbonization period owing to bond breakage at the edges of the planar structures. These electrons are resonance stabilized. Studies by Harker *et al.* (1961) indicated that oxygen interacts with these electrons to form oxygen complexes on the surface. The only means by which this oxygen can be removed is as oxides of carbon by degassing at high temperature.

Oxygen, one of the major noncarbon constituents of active carbon, constitutes 2 to 25% by weight of this material, the exact amount present depending upon the temperature and method of activation (Wolff, 1959). The temperature of activation ranges from 400° to 1200° C., and the oxygen content decreases with increasing temperature of activation (Garten and Weiss, 1957a). Heating carbon at a temperature of 1000° to 1200° C. in a high vacuum removes nearly all of the oxygen from the carbon surface, usually as oxides of carbon. For this reason oxygen is thought to exist in structures on the surface of the microcrystallite or between carbon planes near the surface of the microcrystallite (Garten and Weiss, 1955).

The presence of oxygen complexes on the surface of the carbon affects the sorptive properties of this material in that they tend to increase the polarity of the surface (Barrer, 1966). In aqueous solution, therefore, a stronger solvent-active carbon bond must be broken before sorption of the sorbate can occur if oxygen complexes exist at the carbon surface. Excluding any specific oxygen complex-sorbate interaction, increased polarity decreases the quantity of nonpolar sorbate removed from solution by the carbon. For a polar sorbate, the oxygen complex-sorbate interaction usually is stronger, compensating, at least in part, for the added energy required to desorb water. Kipling (1957) discovered that oxygen on the surface of carbon affects the specificity of sorption from an organic, binary liquid solution. As indicated previously, Kipling and Shooter (1966) reported that iodine apparently does not adsorb on that portion of the active carbon surface

covered with oxygen sites, but does adsorb on the part of the surface covered with hydrogen sites. These authors also indicate that the normally strong lateral interactions of adsorbed iodine molecules appear to be lessened in the presence of the oxygen, thus preventing attainment of the extent of uptake realized in the absence of surface oxygen. An additional consideration is that sorbates which have a natural tendency to combine with oxygen probably sorb more easily on oxygenated surfaces than they do on nonoxygenated surfaces.

Oxygen can be added to an active carbon in one or more of three principal ways. If the starting material contains oxygen, this may become incorporated into the microcrystallite surface structure during the manufacture of the carbon (Garten and Weiss, 1955). If the starting material is a carbohydrate, for example, heating will cause condensation and cyclization of the carbohydrate with the inclusion of an oxygen atom in the ringed structure as an ether oxygen. As a second possibility, oxygen can be sorbed on active carbon at room temperature. Part of the oxygen added in this manner can be evacuated at room temperature—this phenomenon being known as “the reversible effect”—while another part requires evacuation at temperatures in excess of 1000° C. (Harker *et al.*, 1961). The latter phenomenon, which has been studied by electron spin resonance methods, is known as “the surface oxide effect.” Thirdly, oxygen can be chemisorbed on the surface of the active carbon during treatment with oxidizing agents. As previously indicated, the principal oxidizing gases in the activation process are air, steam, and carbon dioxide. These three gases form oxygen complexes at the surface of the carbon which can be removed—as carbon monoxide, carbon dioxide, and water vapor—only by degassing at very high temperatures (Hassler, 1963; Puri *et al.*, 1958). Treatment of active carbon with chemical oxidizing agents in aqueous solution also leads to the chemisorption of oxygen on the surface of the carbon (Puri *et al.*, 1958, 1960, and 1961).

Characterization of Oxygen Surface Structures

Because of their numbers and their probable effects on the sorption process, oxygen complexes on the surface of carbon merit careful consideration. An excellent review of this topic has been given by Boehm (1966); anyone contemplating further work in this area should consult this review.

One of the principal methods for study of the nature of oxygen structures on carbon has been by simple acidimetric-alkalimetric titrations, and major interest has focused on the very important variable of temperature of activation (Boehm, 1966; Garten and Weiss, 1957b). Garten and Weiss (1957b) have provided an excellent review on the findings of such research, and these may be summarized briefly as follows:

Carbon activated at 400° C. (L-carbon) will sorb base but not acid from aqueous solution while carbon activated at 800° to 1000° C. (H-carbon) will sorb acid but not base.

Carbon activated at intermediate temperatures will sorb both acid and base.

Capacities for both acid and base are usually in the milliequivalent per gram range, but this value depends on the substances added to the carbon during the activation process.

Similar to ion exchange resins with basic and acidic functional groups, respectively, H-carbons produce a basic pH in solution, while L-carbons yield an acidic solution pH

(Garten and Weiss, 1957b). Since no acid or base can be extracted from the solution after contact with the carbon, the conclusion is made that surface structures are responsible for this phenomenon. Electrokinetic studies have indicated that H-carbons exhibit a positive surface potential, as opposed to a negative surface potential for L-carbons. However, unless care is taken to cool H-carbons in an inert atmosphere after activation, formation of structures which change the potential from positive to negative does occur. The presence of inorganic constituents at the surface may also affect the potential to the point of reversing its sign from that which might be expected on the basis of the activation temperature.

A negative potential for L-carbons is consistent with the presence of surface acids, while the existence of a positive potential for H-carbons requires further consideration. Garten and Weiss (1957a and 1957b), using various techniques for the study of L-carbons, have concluded that surface acids responsible for the sorption of alkali from aqueous solution consist of at least three fundamental types: phenol; *n*-lactone; and *f*-lactone—the type present in fluorescein and phthalein dyestuffs (Garten *et al.*, 1957). The relative proportions of these three groups vary with the method of preparation of the active carbon.

In determining the total number of acid groups present on L-carbons by alkalimetric titrations, Garten *et al.* (1957) noted that the titration curves closely resembled the type obtained for weak acids and were comparable with that for titration of a phenolic functional group ion exchange resin. These observations point to the possibility of phenolic surface structures, as illustrated in Figure 2. By way of additional evidence, a certain proportion of the acidic groups have been methylated with diazomethane, but the methoxyl group thus introduced resists hydrolysis when treated with boiling dilute acid. This behavior is characteristic of the phenolic structure (Garten *et al.*, 1957; Boehm, 1966). Conversely, a portion of the total number of acidic groups have resisted methylation with diazomethane, while supplementary infrared spectroscopy studies have produced data consistent with the postulation that these groups are of the *n*-lactone type given in Figure 3, with an absorption band at 1710 cm^{-1} .

A third fraction of the acidic groups on L-carbons was methylated with diazomethane, but with the methoxyl group thus formed being hydrolyzable in dilute boiling acid (Garten *et al.*, 1957). Carbon compounds which have phenolic groups in association with lactone groups, as in fluorescein or phthalein dyestuffs, act similarly. Figure 4 gives illustration of the structure of such lactones, called *f*-lactones, as well as some of the reactions of this group (Garten *et al.*, 1957). The infrared data referred to previously have also revealed an absorption peak at 1750 cm^{-1} , consistent with the presence of *f*-lactones.

While simple alkalimetric titration has been used rather extensively for measurement of the total number of acid groups present on carbon, some questions have been raised as to the quantitiveness of this procedure. For example, Studebaker (1963), using sodium aminoethoxide in ethylene diamine as a titrant and comparing his results with those obtained by NaOH-titration of active carbon in aqueous solution, has discovered that alkalimetric titration determines only about 68% of the total acidity as measured by the aminoethoxide titration.

Quinone groups are also known to be present on the surface

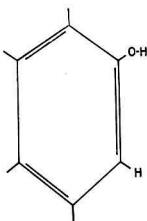


Figure 2. A phenolic surface structure (Garten and Weiss, 1957b)

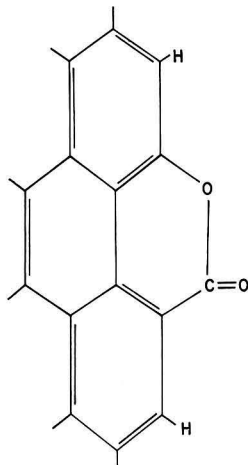


Figure 3. A *n*-lactone surface structure (Garten and Weiss, 1957b)

of active carbon (Garten and Weiss, 1957b and 1961; Studebaker, 1961). An H-carbon cooled in nitrogen gas after activation does not sorb base, but reduction of the H-carbon with sodium borohydride develops base sorbing properties (Garten and Weiss, 1961; Studebaker, 1961). This observation can be explained in terms of quinone reduction to hydroquinone. Hallum and Drushel (1958) also found polarographic evidence for quinones. Reduced quinones, or hydroquinones, might be expected to behave as phenols when treated with diazomethane and thus would be included in the phenolic fraction given by the method of analysis used by Garten and Weiss.

Although a carbon activated at a temperature of 800° to 1000° C. will sorb acid, evacuation at the temperature of activation followed by cooling in an inert atmosphere will so affect the carbon that it will not sorb acid from a deaerated solution until oxygen is admitted (Garten and Weiss, 1957a). Indeed, an exponential relationship exists between the acid sorbed and oxygen partial pressure for the range of 0 to 20 mm. of Hg. Kolthoff (1932) discovered that hydrogen peroxide is released by carbon to a solution from which acid is adsorbed (Garten and Weiss, 1961). Garten and Weiss (1957a), on the basis of this phenomenon, propose the presence of chromene (benzpyran) groups on the H-carbon surface. As illustrated in Figure 5, this structure contains an activated $>CH_2$ or $>CHR$ group which can react with a strong acid and oxygen (Wawzonek, 1950). There is much difficulty

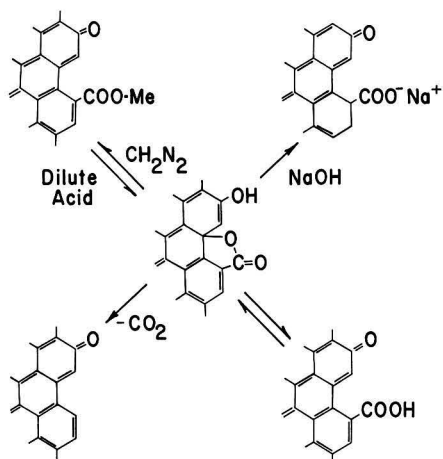


Figure 4. Some reactions of fluorescein-type lactones (Garten *et al.*, 1957)

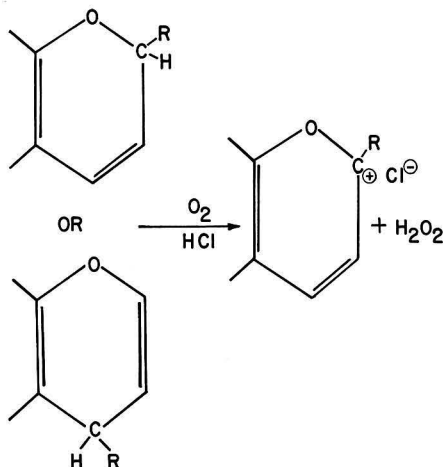


Figure 5. The chromene-acid reaction (Garten and Weiss, 1957a)

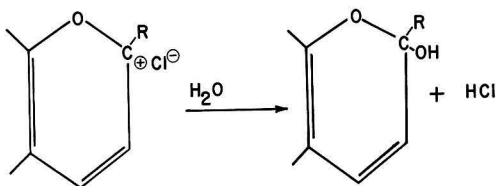


Figure 6. Hydrolysis of the carbonium ion (Garten and Weiss, 1957a)

in establishing the stoichiometry of this reaction, however, because active carbon also catalyzes the breakdown of the hydrogen peroxide (Garten and Weiss, 1957a).

The carbonium ion formed by acid reaction with the chromene group, as shown in Figure 5, will hydrolyze readily in water to form the chromenol group illustrated in Figure 6, a weakly basic group having a dissociation constant of 10^{-11} (Sondheimer, 1953). The fact that the carbonium ion tends to associate so strongly with a negative ion could account for the fact that sorbed acid is very difficult to wash from carbon (Garten and Weiss, 1957a).

In addition to the evidence for chemisorption and the chromene groups, there is also strong evidence that some physical sorption of acid takes place. Garten and Weiss (1957b) have shown that a portion of the sorbed acid on an acid-saturated carbon can be displaced by strongly adsorbed organic molecules. The assumption is made that the physically sorbed acid can be displaced and the chemisorbed acid can not. By this means, an approximation can be made of the number of chromene groups present on the carbon surface. The relative proportion of the quantity of acid physically sorbed to that chemically sorbed again depends on the method of preparation, especially the length of time the carbon is activated.

Discussion

An attempt was made to describe an elementary conceptual model for explanation of some surface properties of active carbon. In the development of this model, it has been necessary to examine the basic structural unit of active carbon, the microcrystallite, and those factors which affect its formation during the manufacturing process. Production variables such as raw material, temperatures of carbonization and activation, additives used for catalysis of carbonization and activation or for the development of specific sorptive properties all seem important in establishing the course of formation of the microcrystallite, and thus the active carbon surface.

Pore surfaces of active carbon appear to consist principally of either the planar or the edge surfaces of the microcrystallite. The planar surfaces are relatively homogeneous, but the edge surfaces are heterogeneous, quite probably covered with oxygen- and hydrogen-containing functional groups. Some of the oxygen complexes appear to be highly reactive with certain inorganic species in aqueous solution, particularly acids and bases. This interaction can be especially significant for active carbons having appreciable quantities of surface oxygen, since it probably results in changes in the nature of the pore surface.

Ash content, which is appreciable for most commercial carbons, might also be expected to affect markedly the nature of the active carbon surface if the inorganic species are distributed over the internal surface of the pores. If the ash is localized in specific vacancies rather than distributed over the pore interior, however, the sorptive properties are likely to be affected very little.

The purpose of this initial model is to set forth some of the more significant interfacial factors and mechanisms to be considered in interpretation of sorption phenomena associated with active carbon in aqueous solutions and to provide a basis for further research aimed at more thorough delineation of sorption processes.

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Ion Exchange Processes for the Reclamation of Acid Mine Drainage Waters

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■ A 3000-p.p.m. (as CaCO_3) synthetic acid mine drainage water (AMD) may be processed to yield a water of quality suitable for industrial, agricultural, and domestic purposes. A basic process, possessing considerable flexibility, has been developed, which our laboratory studies show to be practical. It is based on the use of the conventional gel anion exchange resin, Amberlite IRA-68, which, used in a column operation, functions in the bicarbonate cycle. The effluent water is aerated and subsequently clarified to give useful water, whose quality may be further improved through lime softening prior to clarification. In the clarification step, improved clarification and sedimentation rates may be obtained using an anionic polyelectrolyte such as Primafloc A-10.

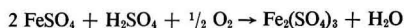
The discharge of acid mine drainage (AMD) waters from coal mines has received considerable attention within recent years. The seriousness of the problem is reflected by numerous laws being enacted on federal, state, and municipal levels. Under the current Pennsylvania Clean Streams Laws, after January 1, 1967, discharge of AMD waters into streams or other waterways is limited to waters that have an iron content below 7 p.p.m. and a pH between 6 and 9. It is estimated that at least 80% of all the mine water effluents in Pennsylvania must be subjected to some sort of treatment before discharge to meet state requirements. The mine water drainage problem is nothing new; it has existed ever since coal mining operations were first begun several centuries ago. The AMD waters present a serious pollution problem which has been increasing because of the existence of an ever larger number of mines, operational and abandoned in the coal mining regions. In effect, the problem is not limited to the United States. Besides Ohio, West Virginia, and Pennsylvania, Western Europe (Wales, the Ruhr, etc.) is plagued with a similar problem. If one were to add to the list the coal mining regions located in the Eastern European countries, the world-wide seriousness of the pollution problem that exists would be greatly magnified. In the Pennsylvania area alone, close to 1.4 billion gallons of acid mine waters are discharged daily.

The extent to which AMD waters become a source of pollution is variable. Though it is difficult to define a typical mine water, one feature common to practically every mine water is its sulfate content. Both acidic and alkaline mine drainage waters occur, though acid waters predominate and cause the greatest inconveniences. The presence of sulfate in AMD waters arises principally from the oxidation of inorganic sulfur-containing substances found in the seams of the mines;

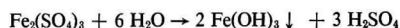
pyrite (FeS_2) is one of the principal constituents. When the pyrites come into contact with water in the presence of air the following reaction takes place:



Upon being discharged into streams, further oxidation unavoidably occurs:



The ferric sulfate so produced hydrolyzes readily (pH 3) to give:



The ferric hydroxide from the hydrolysis reaction is insoluble and is deposited along banks and beds of streams. The sulfuric acid from the hydrolysis reaction then becomes the main source of pollution. It reduces the natural alkalinity of streams and may damage aquatic animal and vegetable life. The pH of the waters is also decreased and there usually is an accompanying increase in the total water hardness. Consequently, water treatment costs are increased if these waters are processed for domestic or industrial use.

The concentration and types of ions found in AMD waters depend on the geological composition of the coal seam. Among other factors, volume and residence time of the waters in the mines, the original ionic composition of the waters before entering the mines, and flow rate become important variables influencing the compositional character of the waters. Besides ferrous ions, originating from the pyrites, AMD waters usually abound in Ca^{+2} , Mg^{+2} , and Al^{+3} . Also found in lesser quantities are manganese and silicate ions. The free mineral acidity of "acid" mine waters, contrary to general belief, is very low, if any acid is present. The acidity values usually reported in reference to a particular AMD water are in actuality a measure of the acidity contributed to the waters by the total dissolved ionic species and not solely of the dissolved free acids.

Methods for Treating AMD Waters

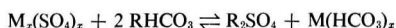
Numerous methods and approaches have been suggested, and some practiced. Recognizing the active role of oxygen (oxidation) in polluting the mine waters, the technique of sealing off abandoned mines (mine sealing), so as to exclude oxygen from the mines, has been practiced with varying degrees of success. Though oxidation is retarded and minimized in many instances, the technique has not generally been effective, especially where the coal seam is above drainage level. Methods that probably have received the greatest attention in recent years are based on the chemical neutralization of the

AMD waters themselves. Neutralization techniques, in general, leave much to be desired. Besides the cost aspect, the processed waters are suitable for neither industrial nor domestic use. Neither the sulfate nor the calcium content of the AMD water is reduced to any significant degree. Actually, in most cases, if lime is employed, the calcium content increases because of the solubility of CaSO_4 . Most neutralization processes only reduce the acidity, iron, and heavy metal content of the mine water, making it acceptable for discharge into streams, thus satisfying state requirements.

Since iron in acid mine water contributes heavily to pollution, several investigators have been concerned principally with the removal of iron rather than total or partial deionization of the acid mine waters. Simpson and Rozelle (1965) briefly discussed methods of removing iron from solution: precipitation (neutralization), electrolysis, aeration-filtration, and ultrasonic methods. They also investigated the use of ozone on both synthetic solutions and actual AMD waters. A combination ozone-activated carbon process is currently in use for removing iron and manganese from Rhine river water (Schenk, 1962). Treatment with ozone oxidizes iron(II) to (III) and manganese to permanganate. A layer of activated carbon is then used to filter out the hydrous iron(III) oxide and reduce the permanganate to dihydroxymanganese(IV) oxide, which may also be filtered out. The iron and manganese oxides can then be backwashed from the activated carbon into a settling basin. Lowell *et al.* (1965) have also taken the neutralization approach, suggesting the use of coal, fly ash, red dog, preparation plant refuse, waste products from the lime-consuming industries, and limestone for this purpose. Two United States patents (Magill, 1941; Rodman, 1933), which were issued in the middle thirties and early forties, make claim to the use of materials comprising coal and carbonaceous coke alone or in conjunction with inorganic chemicals for treatment of waters to render them potable. Using these coal materials, Lowell *et al.* found that the pH of acid mine waters could be increased and the acidity and iron content decreased. However, the response of different coals varied widely and sulfur was not removed from the aqueous system despite changes in pH, acidity, or iron content. Other methods such as flash distillation and electro dialysis have been suggested, but the practicability and economics of such processes are highly questionable.

Ion Exchange Process

The use of weak base resins such as Amberlite IRA-68, operated conventionally in the free base cycle, is not a practical system for processing an AMD water, since hydrous metal oxide is unavoidably precipitated in the resin beds during the anion exchange neutralization. On the other hand, the use of the weak base resin operated in the bicarbonate cycle circumvents this problem. In the process, advantage is taken of the fact that the metal sulfates, which usually represent almost the entire soluble anion content of typical AMD waters, are readily converted to the soluble bicarbonates, with subsequent deposition of a significant portion of the metallic ions as the insoluble hydrous oxides by the ion exchange of the AMD waters with Amberlite IRA-68 operated in the bicarbonate cycle. The following conversion occurs:

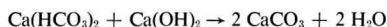


where

R = Amberlite IRA-68

M = Fe^{+2} , Al^{+3} , Mn^{+2} , Ca^{+2} , Mg^{+2} , etc.

Upon aeration of the effluent waters, carbon dioxide is expelled, precipitating iron, aluminum, and manganese as the insoluble hydrous oxides. A certain portion of the calcium and magnesium is also coprecipitated or occluded with the hydrous oxides as CaCO_3 and $\text{Mg}(\text{OH})_2$. Ferrous and any other easily oxidizable ions present in solution are also oxidized, while the bulk of the calcium and magnesium remains solubilized as the bicarbonates. In essence, what remains after aeration is a bicarbonate water (pH 8.0 to 8.2) containing calcium and magnesium hardness. Should further deionization be required, a cold lime-softening treatment at this point is rather effective. Lime treatment of the aeration waters results essentially in the following reaction:



After lime treatment, a complete deionization will not be achieved, since CaCO_3 and $\text{Mg}(\text{OH})_2$ both have limited solubilities in water. After aeration or after lime treatment, should this step be made an integral part of the process, clarification of the waters is facilitated through the use of an anionic polyelectrolyte. The over-all process is diagrammatically represented in Figure 1.

As in other AMD reclamation processes, the problem of sludge disposal is always present. The goal then is to obtain as low a volume of sludge and as great a recovery of water as possible. It has been demonstrated, at least on a laboratory scale, that the volume of sludge produced by the proposed ion exchange process is substantially less than obtained during the lime-neutralization treatment of an identical synthetic AMD water. As a result, even though the ion exchange process does not completely eliminate the sludge problem, it does go a long way toward reducing the disposal problem. Since a smaller amount of sludge is produced, less lagooning area will be necessitated, should lagooning be a preferred disposal practice. Should the sludge be combined with coal refuse, the coal refuse requirements will be considerably reduced, as would be the abandoned mine space required for disposal by this alternative means.

Experimental

Amberlite IRA-68 (Rohm and Haas Co.) is the anion exchange resin of choice in the process, since it may be effi-

Table I. Synthetic AMD Water

pH	3.1
Sp. resist., ohm cm.	310
Ca^{+2} , p.p.m. as CaCO_3	964
Mg^{+2} , p.p.m. as CaCO_3	480
Fe^{+2} , p.p.m. as CaCO_3	895
Al^{+3} , p.p.m. as CaCO_3	556
Mn^{+2} , p.p.m. as CaCO_3	91
Free mineral acidity, p.p.m. as CaCO_3	118
SO_4^{-2} , p.p.m. as CaCO_3	3104

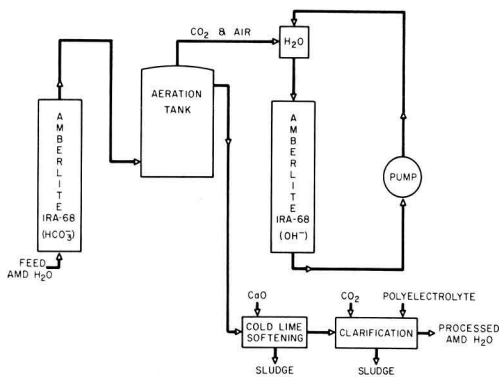


Figure 1. IER process for treatment of AMD waters

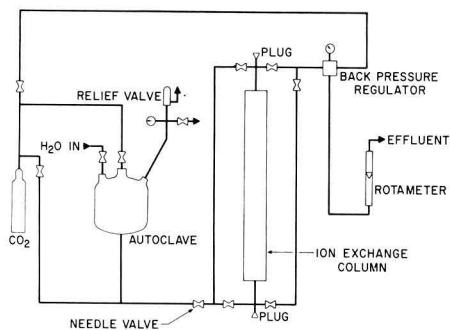


Figure 2. Schematic drawing of pressurized ion exchange system for treatment of AMD water

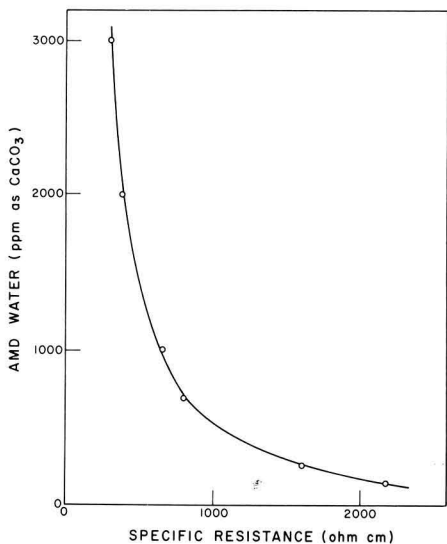


Figure 3. Standard curve relating specific resistance and total dissolved solids of synthetic AMD water

ciently converted to the bicarbonate form using a carbonated water. It is a weak polyamine anion exchange resin. The particular resin employed in our studies had a volume exchange capacity of 1.63 meq. per ml.

As the working solution in the process studies, a synthetic AMD water was prepared which was considered to be fairly representative of typical AMD waters commonly encountered in the field. In Table I are listed the compositional features of the water, pH, and specific resistance.

Stability of the water was excellent for as long as 3 to 4 weeks if the water was initially prepared to contain some free mineral acidity. No detectable change in pH, specific resistance, or total dissolved solids was apparent over this period. A water prepared without any significant free mineral acidity (pH 3.6), on the other hand, showed considerable instability after only a few days, then became discolored (yellow-brown) and considerable finely dispersed turbidity particles were evident.

Apparatus

Since use of pressurized carbonated water allows a greater solubilization and effective utilization of carbon dioxide during the carbonation step of the alkalization operation, a pressurized ion exchange unit was used to convert Amberlite IRA-68 to the bicarbonate form and alkalize the acid mine drainage waters. The pressurized alkalization unit is schematically diagrammed in Figure 2. The configuration of the equipment allows either conventional or upflow operation of the ion exchange column during the exhaustion cycle and for either internal (carbonation) or external (NH_4OH) regeneration. The column was approximately 36 inches long and had an internal diameter of 1 inch. It was adapted with two stainless steel fine wire mesh screens at both ends. To minimize obstruction of the screen openings and loss of resin, the resin bed consisted of a +40-mesh (U.S. Standard sieve) resin cut of Amberlite IRA-68. Using a 200-ml. resin bed volume, enough head room was available in the column to allow for at least a 100% expansion of the bed during the upflow exhaustion operation. When the resin needed to be regenerated with NH_4OH , the column could be isolated from the rest of the system by manipulating the appropriate valves. Two plugs at the end of the column were removed and the ammonia regeneration could then be performed by gravity. To convert the resin to the bicarbonate form, 2-liter quantities of water were introduced into the autoclave, saturated with CO_2 gas at 75-p.s.i. pressure, and then passed (downflow) through the pressurized column using a 50-p.s.i. CO_2 head pressure. Once regenerated, the AMD water could be introduced into the autoclave and in turn passed upflow through the column under a 50-p.s.i. CO_2 head pressure.

Analysis

The unit operations of the over-all process were followed by pH, specific resistance, alkalinity, or a combination of these. Specific resistance and alkalinity measurements were particularly useful in checking the effectiveness of the treatments at various stages of the process. Specific resistance measurements gave an approximate measurement ($\pm 10\%$) of the total dissolved solids still remaining in the processed waters. A plot of specific resistance vs. total dissolved solids (as CaCO_3) (Figure 3) was prepared by making appropriate dilutions of the synthetic AMD water with deionized water and then

measuring the specific resistance of the diluted samples. Alkalinity measurements gave a means of following the extent of the $\text{SO}_4^{2-} \rightarrow \text{HCO}_3^{-1}$ conversion during the alkalization step.

Total cations remaining in the final processed waters were obtained by an ion exchange procedure by passing a water sample through a small column containing Amberlite IR-120 (H), a sulfonic cation exchange resin. After the effluent water from the column had been collected, the acidity generated was titrated to the methyl orange end point with standard NaOH and the titration value in turn related to the metal sulfate (and carbonate) content of the original sample. A second sample of the processed water was titrated with acid (M.O. end point) to obtain the metal bicarbonate alkalinity. The total cations in the processed water were equal to the summation of these two values. Total hardness and total calcium were determined by the standard EDTA titration. Total magnesium was obtained from the difference between the two values and consequently magnesium values reported may not be fully reliable. Iron, aluminum, and manganese were measured using specific spectrophotometric procedures. Though sulfates were not determined *per se*, the maximum level present in a particular water could be estimated, being no greater than the total cations determined by the ion exchange technique using Amberlite IR-120 (H).

Process Studies

In the initial phase of the study, Amberlite IRA-68 was used to convert the metal sulfates of the synthetic AMD water to the soluble bicarbonates, using the pressurized unit described. Prior to treatment of the AMD water, the Amberlite IRA-68 (free base form) was converted to the bicarbonate form using an excess volume [(in our laboratory studies, 30 bed volumes (BV)] of D.I. (deionized) water, previously saturated with CO_2 at 75 p.s.i. After conversion of the resin to the bicarbonate form, alkalization ($\text{SO}_4^{2-} \rightarrow \text{HCO}_3^{-1}$ conversion) of the AMD water was carried out upflow at a flow rate of 2 gallons per cu. foot per minute. The upflow operation minimized the deposition of precipitates that could have formed had some of the resin sites still have been in the free base form after the carbonation step. The effluent waters emerging from the ion exchange column were collected and aerated vigorously for 1 hour or less—that is, until the pH of the slurries rose above 8 and remained essentially constant with continued aeration. The red-brown liquid slurries that resulted were clarified at this point or processed further by subjecting them to a lime-softening treatment.

In Table II are listed alkalinity data obtained during the exhaustion cycle and other pertinent information pertaining to a typical run. The fact that the level of alkalinity formed during the run was less than the influent concentration does not mean that the conversion was incomplete; however, as the effluents were collected some decomposition of the ferrous bicarbonate occurred [$\text{Fe}(\text{HCO}_3)_2 \rightarrow 2 \text{CO}_2 + \text{Fe}(\text{OH})_2$], resulting in a loss of alkalinity.

Three composite samples of the fractions collected from the Amberlite IRA-68 column were prepared. Fraction 1 was a composite of the first 28 bed volumes, Fraction 2 the first 32 BV, and Fraction 3 all 36 BV collected. These samples were then further processed (aeration, lime softening, and clarification-sedimentation). The samples were aerated for 75

minutes, and then limed for 1 hour at room temperature, using a quantity of lime corresponding to the residual M.O. alkalinity present in samples of the clarified waters after the aeration operations. Evaluation data were obtained for the aerated and lime-softened slurries after clarifying each with the aid of a few parts per million of Primafloc A-10. The data are reported in Table III.

The effect of using different levels of lime during lime softening of the aerated slurries was investigated. The completeness of the liming operation was determined when quantities

Table II. Alkalization of AMD Water with Amberlite IRA-68 (HCO_3^-)

Resin bed volume. 200 ml. Bed height. 18 inches	CO_2 driving pressure. 50 p.s.i. Exhaustion flow rate. 2 gal./cu. ft./min.	M.O. Alkalinity, P.P.M. as CaCO_3
Bed Volumes Collected		
1-4 ^a		1350
5-8		2250
9-12		2230
13-16		2230
17-20		2280
21-24		2290
25-28		2290
29-32		1100
33-36		0

^a Contains approximately 1 1/2 BV of sweetening-off carbonated water from column and lines.

Table III. Evaluation Data for Processed AMD Waters

	28-BV	32-BV	36-BV
	Composite Composite Composite		
After aeration			
pH	8.45	8.30	8.0
Sp. resist., ohm cm.	1320	1260	880
M.O. alkalinity, p.p.m.			
as CaCO_3	420	420	300
SO_4^{2-} , p.p.m. as CaCO_3	0	...	<630
Ca^{+2} , p.p.m. as CaCO_3	390	420	680
Mg^{+2} , p.p.m. as CaCO_3	50	40	40
After lime softening			
pH	8.80	8.65	8.20
Sp. resist., ohm cm.	3600	2000	1160
M.O. alkalinity, p.p.m.			
as CaCO_3	180	170	70
SO_4^{2-} , p.p.m. as CaCO_3	0	<125	<375
Ca^{+2} , p.p.m. as CaCO_3	160	290	470
Mg^{+2} , p.p.m. as CaCO_3	5	10	10

Table IV. Processed Amberlite IRA-68 (HCO_3^-) Waters as a Function of Lime-Softening Level

Lime used, % of residual alk. after aeration	25	50	100
pH	8.00	8.10	8.20
Sp. resist., ohm cm.	850	960	1160
M.O. alk., p.p.m. as CaCO_3	280	190	70
M.O. alk. removed, %	18	44	80

Primaflow A-10 Dosage, P.P.M.	Rate, ^a Lb./Ton	Table V. Primaflow A-10 Flocculation Tests		Remarks
		Lb. of Primaflow A-10/1000 Gal.		
		Aerated Composite, 36 BV		
		Aerated Solids, 2600 P.P.M.		
0.5	0.38	0.0042		Small flocs, slight haze
1.0	0.77	0.0083		Fair flocs and settling, sl. haze
3.0	2.31	0.0249		Good flocs and settling, clearer
3.5	2.69	0.0290		Very good flocs and settling; clear
4.0	3.08	0.0332		Optimum, excellent floc and clarity
4.5	3.46	0.0374		Excellent floc and clarity
		Lime-Softened Composite, 36 BV		
		(Lime Used Equivalent to 25% of Measured Alkalinity after Aeration)		
		Limed Solids, 2850 P.P.M.		
0.5	0.351	0.0042		Some fine flocs, sl. haze, good settling
1.0	0.702	0.0083		Large flocs, sl. haze, good settling
1.5	1.053	0.0125		Very good flocs, clear, very good settling
2.0	1.404	0.0166		Optimum, excellent clarity and settling
3.0	2.106	0.0230		Excellent clarity and settling
4.0	2.808	0.0332		Excellent clarity and settling
		Lime-Softened Composite, 36 BV		
		(Lime Used Equivalent to 50% of Measured Alkalinity after Aeration)		
		Limed Solids = 3020 P.P.M.		
0.5	0.331	0.0042		Good flocs, sl. haze, good settling
1.0	0.662	0.0083		Very good flocs, sl. haze, very good settling
1.5	0.993	0.0125		Optimum, excellent clarity and settling
2.0	1.324	0.0166		Excellent clarity and settling
		Lime-Softened Composite, 36 BV		
		(Lime Used Equivalent to 100% of Measured Alkalinity after Aeration)		
		Limed Solids, 3290 P.P.M.		
0.5	0.304	0.0042		Very good flocs, sl. haze, very good settling
1.0	0.608	0.0083		Optimum, excellent clarity and settling
2.0	1.216	0.0166		Excellent clarity and settling

^a Pounds of flocculant per ton of solids

of lime corresponding to 25 and 50% of the residual alkalinity were used (Table IV). Prior to the lime-softening treatments, a clarified portion of the aerated slurry exhibited a pH of 8.0, a specific resistance of 880 ohm cm., and a M.O. alkalinity value of 340 p.p.m. as CaCO₃.

An almost linear relationship exists for the amount of alkalinity removed *vs.* the level of lime employed when lime is used in quantities below the stoichiometric (100%) residual alkalinity value during the lime-softening operations.

Clarification-Sedimentation

During the clarification of the slurries that result from either the aeration or lime-softening step, clarification and sedimentation rates are significantly improved when an anionic polyelectrolyte is employed. Primaflow A-10 (Rohm and Haas Co.) was found to be a most effective flocculant for this purpose. In Table V, flocculation data obtained during treatment of the 36-BV composite of Amberlite IRA-68 (HCO₃) processed AMD water (Table III) are summarized, with data for flocculation tests performed on the aerated slurries with and without lime softening. In the case of the lime-softened slurries, flocculation tests were conducted on the slurries previously lime-softened with quantities of lime equivalent to 25, 50, and 100% of the M.O. alkalinity originally present in the aerated slurries (Table IV). The polyelectrolyte dosages are the levels of flocculant used per total volume of slurry.

During the tests, Primaflow A-10 was used as a 0.1% active (sodium salt) solution in all cases.

Larger optimum dosage levels of Primaflow A-10 are required for the aerated slurries than the limed slurries (Table V). This is to be expected, since the effectiveness of Primaflow A-10, and of most other anionic polyelectrolytes, improves with increased suspended solids content and pH.

Since the existence of a sludge disposal problem is recognized in the case of direct lime neutralization methods for the processing of AMD waters, the amount of sludge resulting during a typical ion exchange resin process run was measured, primarily to ascertain whether the ion exchange resin process offers any improvement over the direct lime neutralization techniques by producing a smaller amount of sludge. Accordingly, 100-ml. volumes of Amberlite IRA-68-treated waters, aerated and lime-softened at various levels with lime, were treated with Primaflow A-10 and allowed to settle in graduated cylinders. For comparison, additional AMD water was treated by the direct lime neutralization method at pH 6.6, 7.3, and 8.2 with subsequent aeration. The aerated slurries (100-ml. volumes) were in turn treated with Nalco 670, a nonionic flocculant especially effective as a settling aid for direct lime-treated AMD waters, and allowed to settle likewise in graduated cylinders.

In Table VI, the time required for 50% of the sludge to settle is recorded along with the per cent volume of sludge that settled out after a 24-hour period.

Table VI. IER and Lime Neutralization Processes Sedimentation Comparative Data

Process	Time, Hr., 50% Settling	Final Sludge Volume, Vol. %
IER		
No lime	<0.30	4.5
50% lime	<0.30	5.5
100% lime	<0.30	6.0
Lime neutralization		
pH = 6.6	≅1.00	23.5
pH = 7.3	≅1.00	24.0
pH = 8.2	≅1.00	26.0

Though some increase in sludge volume resulted with the use of Primaflor A-10 (IER process), the sludge volume obtained was still significantly less than found through direct lime neutralization. In fact, a few laboratory scale continuous runs have demonstrated that if the aerated waters from the ion exchange process are transferred to a settling tank and only the overflow waters flocculated using Primaflor A-10, the volume of sludge that results (settling tank and flocculation tank) is essentially equal to the sludge volume obtained had no flocculant been employed (approximately 3%).

Regeneration

The Amberlite IRA-68 resin, previously exhausted during the treatment of 36 BV of AMD water, was subsequently regenerated. To convert the resin back to the free base form, a quantity of 1N NH₄OH solution was used which corresponded to a 50% excess of the resin exchange capacity utilized during the SO₄⁻² → HCO₃⁻¹ exchange. To obtain an accurate measurement of the capacity realized during the treatment of the AMD water, the total regeneration effluent consisting essentially of NH₄OH and (NH₄)₂SO₄ was collected. By passing an aliquot sample through a small column of Amberlite IR-120(H) the amount of H₂SO₄ generated was determined by titration and related directly to the SO₄⁻² content displaced from the Amberlite IRA-68 during the ammonia regeneration.

After converting the resin to the bicarbonate form, a second alkalization cycle was performed to ascertain whether or not the resin had been fully regenerated. In Table VII, the data obtained for the two alkalization runs are compared. The column capacities reported were measured experimentally using the ion exchange technique described.

Though lime may not be used directly to regenerate the sulfate-exhausted Amberlite IRA-68 due to CaSO₄ formation, it may be used to recover ammonia from spent regenerant solution. The recovered ammonia, containing from 1.0 to 1.5 grams of soluble CaSO₄ per liter, may be reconstituted and used effectively for additional regenerations. In Table VIII are reported alkalization data for both fresh resin and resin regenerated with lime-recovered ammonia.

Chemical Characteristics of Processed Water

The processed water obtained from several additional treatments of the AMD water contained from 150 to 600

Table VII. Comparative Data on Alkalization of AMD Water Using Amberlite IRA-68 (HCO₃⁻)

Bed Volumes Collected	Alkalization Cycle	
	1 Alkalinity, P.P.M. as CaCO ₃	2
1-4	1350	1490
5-8	2250	2290
9-12	2230	2270
13-16	2230	2230
17-20	2280	2280
21-24	2290	2280
25-28	2290	2280
29-32	1100	1390
33-36	0	0
Column capacity, kgr./cu. ft. ^a	33.9	33.0

Evaluation of Processed H₂O (after Aeration, Lime Softening, Clarification) (32-BV Composite)

pH	8.65	8.20
Sp. resist., ohm cm.	2000	1650
M.O. alk., p.p.m. as CaCO ₃	170	200
SO ₄ ⁻² , p.p.m. as CaCO ₃	<125	<130
Ca ⁺² , p.p.m. as CaCO ₃	290	420
Mg ⁺² , p.p.m. as CaCO ₃	10	20
Total hardness, p.p.m. as CaCO ₃	300	440

^a Kilograins per cu. foot.

Table VIII. Comparative Data on Alkalization of AMD Water Using Amberlite IRA-68 (HCO₃⁻) Regenerated with Fresh and Reconstituted Lime-Recovered NH₄OH

Bed Volumes Collected	Alkalization Cycle	
	Fresh Resin Alkalinity, P.P.M. as CaCO ₃	Regenerated Resin
1-4	1700	1800
5-8	2200	2350
9-12	2280	2280
13-16	2250	2290
17-20	2290	2280
21-24	2280	2310
25-28	2300	2270
29-32	1380	1420
33-36	0	0

Table IX. Evaluation of Selected Processed Water Samples for Metallic Ions

Sample	Treatment	P.P.M.		
		Al	Fe	Mn
1	Amberlite IRA-68 (HCO ₃ ⁻) treated; aerated, no lime	0.2	0.12	<0.05
2	Amberlite IRA-68 (HCO ₃ ⁻) treated; aerated, limed	0.5	<0.1	<0.05

p.p.m. of dissolved solids (as CaCO₃) in the case of waters clarified after aeration or after further processing (lime softening). In all cases, the predominant ions remaining solubilized in the processed waters were calcium, bicarbonate, and carbonate. Magnesium ions were present at a much lower concentration than calcium ions. When the alkalization treatment was not 100% complete, the processed waters contained varying quantities of sulfate ions. Processed waters characterized by pH values greater than 8.5 (due to excess lime during lime softening) also exhibited small levels of soluble calcium hydroxide. Essentially no iron, aluminum, or manganese was present, based on the analysis of a selected series of processed water samples. Values were well below 1 p.p.m. in the case of all three ions. Analytical data pertinent to typical samples have been tabulated in Table IX.

The samples in Table IX refer to the 36-BV composite of AMD water previously treated with Amberlite IRA-68 (HCO₃⁻) (Table III). When the 28- and 32-BV composites of the same run were analyzed, aluminum was absent; the iron was less than 0.01 p.p.m. and the manganese less than 0.05 p.p.m.

Cost Estimate

The operating costs of the AMD water purification process based on the use of Amberlite IRA-68 have been calculated for plant sizes of 100,000 and 1,000,000 gallons per day.

For calculation purposes, it was assumed that the AMD had a 3000-p.p.m. SO₄⁻² (as CaCO₃) content and that a 34-kgr. (as CaCO₃) per cu. foot capacity would be realized during alkalization. For the lime-softening operation, cost calculations, with regard to consumption of lime, were based on the assumption that approximately 15% (400 to 500 p.p.m.) of the influent SO₄⁻² content would still be solubilized as alkalinity in the aerated slurries after aeration and an equivalent amount of lime corresponding to the residual solubilized alkalinity would be used during lime softening.

In Table X, the costs calculated for each of the individual phases of the operation are listed, including grand total cost values for both the 100,000 and 1,000,000 gallons per day installations.

Since the cost of the chemicals used greatly influences the operational costs, any chemical cost reduction due to availability or other factors will considerably improve the economics of the operation. For example, if CO₂ could be generated from the burning of coal at the actual operational site, the price of CO₂ could be as low as \$20 per ton. Another important factor is the total anion content of the AMD water. With

increased anion content, the length of the alkalization cycle will diminish and therefore more regeneration cycles will be needed per day, increasing daily processing costs. For economic reasons, therefore, the present AMD ion exchange process, based on the use of Amberlite IRA-68, should be limited to AMD waters characterized by anion contents below 4000 p.p.m. as CaCO₃.

Discussion

Since some precipitation may occur during alkalization it has been necessary to operate in an unconventional upflow manner during the ion exchange step. Amberlite IRA-68 has performed remarkably well under these conditions during numerous laboratory runs. No noticeable pressure drop nor deposition of precipitates into the resin bed has been experienced. In addition, essentially theoretical utilization of the resin exchange capacity (33 to 34 kgr. per cu. foot) has been achieved in each instance.

The total cost to process an average AMD water has been calculated to be well within the range of 25 to 50 cents per 1000 gallons, the actual cost depending primarily on regenerant costs, the quality of processed water desired, and the anion content of the AMD waters.

Disposal of the waste regenerant from the ion exchange unit might present a BOD problem unless the regenerant, consisting primarily of ammonium sulfate, can be used as a fertilizer or put to some other use. Recent experimentation has demonstrated that one way of circumventing the problem would be to treat the waste regenerant with lime, forming a CaSO₄ precipitate and NH₄OH. The precipitate would then be combined with the process sludge and the NH₄OH solution re-used during subsequent regenerations.

The process possesses much flexibility and a water of practically any desired quality may be obtained, something that direct lime neutralization methods have not achieved. For example, at a relatively insignificant increase in cost, the processed waters may be completely deionized by further subjecting them to a dealcalization treatment. Amberlite IRC-84, a weak cation exchange resin, is particularly useful for this purpose. In essence, this places the process in a unique position in the spectrum of mine effluent treatment systems now available to the coal mining communities.

Acknowledgment

The authors acknowledge the assistance of Thomas Doherty in conducting the experimental portion of this study.

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Table X. Cost Estimate for AMD Water Reclamation Process

	\$ Cost/1000 Gal.	
	100,000 gal./day	1,000,000 gal./day
Alkalization	0.285	0.246
Carbonation ^a	0.149	0.134
Degasification	0.009	0.003
Lime softening ^b	0.032	0.032
Clarification ^b	0 ^c .014	0.014
Grand total	0.489	0.429

^a Includes CO₂ make-up.

^b Chemicals only, does not include equipment.

Evaluation of Various Silica Gels in the Gas Chromatographic Analysis of Light Hydrocarbons

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■ The separations of light hydrocarbons obtained with columns packed with the following Davison silica gels: Types No. 08, 15, 35, 58, 62, 81, 113, and 950 are described. Experimentally, these silica gels were classified in two groups: high activity silica gels with average pore diameter around 25 Å., and medium activity silica gels with average pore diameter around 150 Å. Light-hydrocarbon chromatograms characteristic of the two groups are shown. The effects of various polar liquid phases and water upon the silica gels of 150-Å. pore diameter are discussed in detail. A system is described that can be used for analyzing C₁ to C₅ paraffins, C₂ to C₄ olefins, and acetylene in automotive emissions and in ambient air. Some of the advantages of using solid adsorbents for such analysis are also discussed.

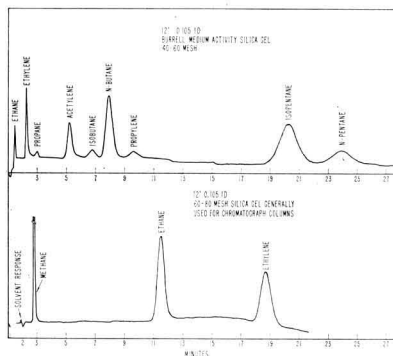


Figure 1. Comparison of silica gels

Gas chromatography is an important tool in air pollution studies and research for the analysis of complex hydrocarbon mixtures. With the proper selection of a detector and column, a precise, quantitative analysis of most hydrocarbons can be made with no interferences owing to other compounds (Altshuller, 1963). In earlier papers, the authors reported a gas chromatographic method for the analysis of light hydrocarbons present in auto exhaust (Bellar *et al.*, 1962) and ambient air (Altshuller and Bellar, 1963). The method required a column packed with a medium activity silica gel (Burrell Co.). This silica gel is no longer available. Chromatograms obtained with silica gels procured from other chromatographic supply sources did not duplicate the separations obtained with the Burrell medium activity silica gel. The separations are shown in Figure 1.

The advantages of the Burrell medium activity silica gel for analysis of light hydrocarbons are demonstrated. According to Kiselev *et al.* (1964), the differences between the two chromatograms may be attributed mainly to the dissimilar pore diameters of the two silica gels. Comparison of the chromatograms with similar chromatograms reported by Kiselev *et al.* (1964) indicates that the average pore diameter of the commercially available silica gel is between 20 and 30 Å.

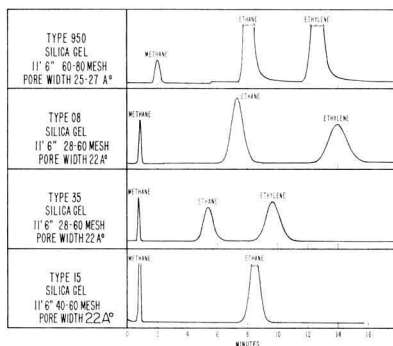


Figure 2. Chromatograms of the narrow pore width Davison silica gels

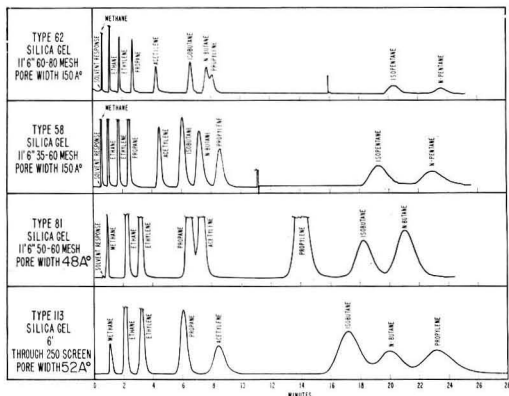


Figure 3. Chromatograms of the large pore width Davison silica gels

whereas that of the Burrell medium activity silica gel is between 100 and 150 A.

Several types of silica gels were provided by the W. R. Grace & Co., Davison Chemical Division, for experimental purposes. The physical properties of these silica gels (Davison Technical Bulletin No. 303) are listed in Table I. Columns were prepared from each of these silica gels, and they were operated under conditions similar to those used for the Burrell medium activity silica gel column with a helium flow rate of 40 cc. per minute at a temperature of 22° C. The resulting chromatograms are shown in Figures 2 and 3. Figure 2 represents the chromatogram obtained with silica gel with average pore diameter of 22 to 30 A. These chromatograms closely resemble those obtained with silica gel commonly sold for use in gas chromatography. Figure 3 shows the chromatograms obtained with silica gels with average pore diameters ranging from 48 to 150 A. The chromatograms for 150-A. silica gel closely resemble those obtained with the Burrell medium activity silica gel.

A wide variety of hydrocarbon analyses can be worked out with proper selection of silica gel pore size. One can also take advantage of the rapid increase in adsorptive effects of the silica gel as a function of the increasing molecular weight of the hydrocarbons.

For example in the 150-A. silica gel chromatogram an excellent analysis of C₁ to C₅ paraffins ethylene, propylene, and acetylene is shown. C₄ olefins eluting past n-pentane are

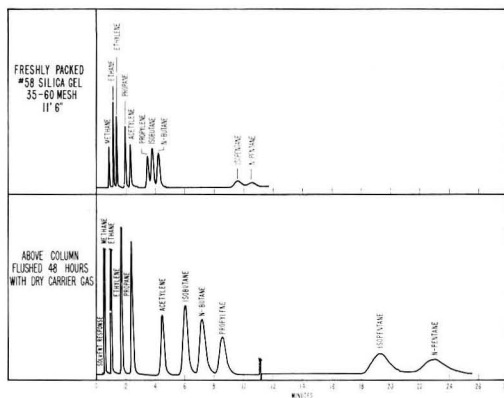


Figure 4. Effect of the loss of volatile matter

Table I. Physical Properties of the Davison Silica Gels Tested

Grade No.	08	15	35	58	62	81	113 ^a	950
Particle size Tyler sieve	12-28	35-60	12-42	35-60	60-200	50-200	Thru 250	60-200
Bulk density, lb./cu. ft.	44.0	42.0	44.0	24.0	25.0	36.0	31.0	46.0
Total volatile % at 1750° F.	5.5	6.5	6.5	4.5	6-8	12.0	12.0	6.5
Surface area, sq. m./g.	750	800	832	300	340	600	550	700
Pore volume, cc./g.	0.40	0.43	...	1.15	1.15	0.70	0.75	0.40
Pore diameter, A.	22	22	22	150	150	48	52	25-30

^a Grade No. 113 silica gel is an impure product containing over 12% alumina (silica gels were supplied by the W. R. Grace Co., Davison Chemical Division).

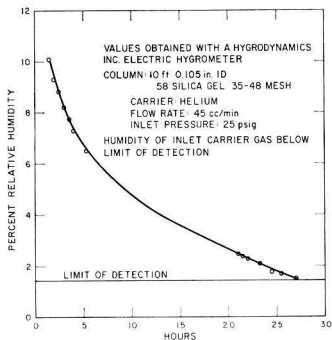


Figure 5. Humidity of the carrier gas at the column exit

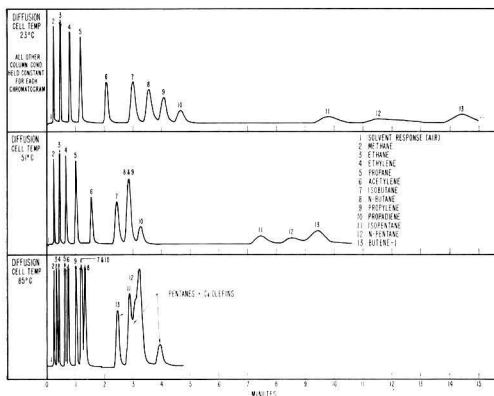


Figure 6. Effect of water in carrier gas upon Type 58 silica gel

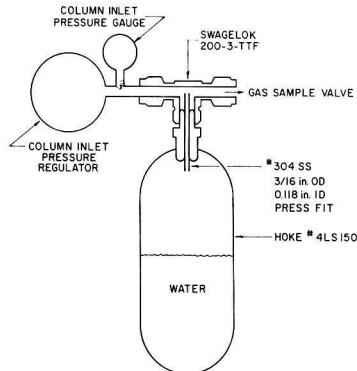


Figure 7. Diffusion cell

doublets with the various isomeric C_6 paraffins. The utility of such complex peaks for quantitative work is doubtful. Column length and silica gel pore diameter can be selected so that the rapid increase in adsorptive effects occurs around normal pentane. Compounds eluting after normal pentane have large half width at their elution time and would be barely detectable because of the dilution effect of the carrier gas. This effect makes backflushing unnecessary and thus increases the number of analyses possible in a given period of time.

When the large pore diameter silica gel columns were conditioned with helium at room temperature, the retention times and retention orders for the various compounds varied (Figure 4). Generally, after 24 hours, a reproducible retention order is established. The retention times remain fairly constant except for acetylene, which slowly migrates toward the isobutane peak. Because of these variations it is impractical to compare relative retention volume values among the various silica gel columns.

Effect of Absorbed Water

The variation of retention times and orders is attributed to the loss in volatile matter that has been absorbed by the silica gel during manufacturing and column packing. Physical properties of the silica gels (Table I) indicated that the percentage of volatile matter driven off at 1750° F. varies between 5.5 and 12%, depending upon grade of silica gel. If the volatile matter is mostly water, anhydrous carrier gas passing through the column would desorb the water until equilibrium between the gaseous and solid phases is approached. This assumption has been experimentally confirmed by two methods. First, the relative humidity of the column exit gas was monitored for 24 hours with an electronic hygrometer (Figure 5). The humidity of the exit carrier gas drops off rapidly with time until the humidity approaches the detection limit of the hygrometer. This change in humidity parallels the changes in retention times throughout the first 24 hours of a column's life. The second method was to contaminate the carrier gas with a trace amount of water, either by passing the carrier gas through a tube filled with various salt crystals containing water of hydration or by means of a water diffusion cell operated at various temperatures. Varying the percentage

of water in the carrier gas gave corresponding variations in retention times and orders (Figure 6).

The use of salt crystals with water of hydration effectively maintained constant relative retention volumes. The main disadvantage is that the crystals must be changed weekly because of their limited water capacity. The water diffusion cell, Figure 7, is now used to maintain constant humidity in the carrier gas. If the various cell parameters are held constant, the relative retention volumes do not change. The water level in the cell is independent of the diffusion rate and needs to be checked only about once every three months to ensure the presence of water. A gas chromatograph operating under the conditions shown in Table II is now used for routine analysis of automotive emissions and for direct sampling of ambient air.

Effect of Absorbed Liquid Phases

Type 58 silica gel was coated with 18 various common liquid phases in an attempt to replace the water in the silica gel pores with a less volatile substance. Figure 8 shows the general effect of the liquid phases tested. The nonpolar liquid phases do not appreciably affect the resulting chromatogram,

Table II. Operating Parameters of Gas Chromatograph for Light Hydrocarbon Analysis

Carrier gas	Helium
Inlet pressure	15 p.s.i.g.
Flow rate	36.4 cc./min.
Column	12-foot 0.105-inch I.D. Type 304 stainless steel
Packing material	Type 58 silica gel 35 to 60 mesh
Column temperature	22° C.
Diffusion cell temperature	22° C.
Diffusion cell orifice diameter	0.118 inch
Diffusion cell orifice length	2.0 inches
Detector	Flame ionization Barber Colman 0.08-inch diameter jet nozzle
Hydrogen flow rate	37 cc./min.
Air flow rate	42 cc./min.
Sample sizes used	1/4, 1.0, 5.0 cc.

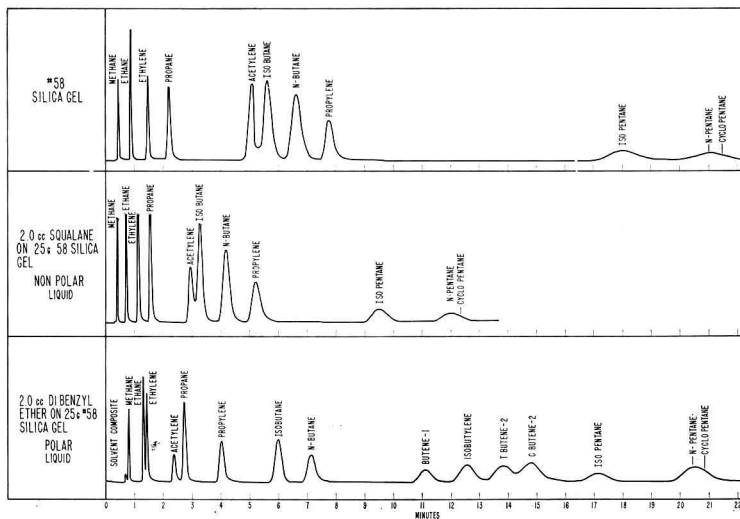


Figure 8. Effect of polar and nonpolar liquids on Type 58 silica gel

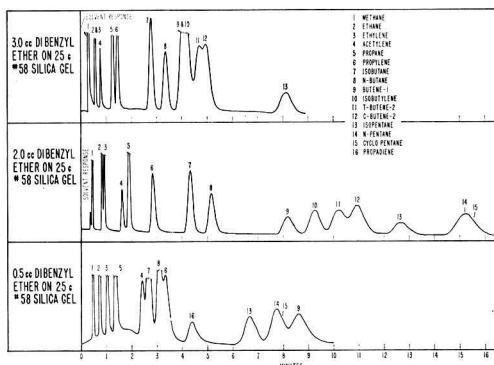


Figure 9. Effect of various amounts of polar liquids on Type 58 silica gel

whereas polar liquids affect the silica gel much the same as water. Figure 9 shows the effect of various amounts of dibenzyl ether applied to Type 58 silica gel. With trace amounts of liquid coating, separations are similar to those obtained with a water diffusion cell. At higher concentrations, the polar liquid greatly reduces some of the absorptive effects of the silica gel and causes elution of hydrocarbon compounds in order of their molecular weights. Identification of the peaks thus becomes much simpler. The column packed with 25 grams of Type 58 silica gel modified with 2 cc. of dibenzyl ether provides a complete butene-1-isobutylene separation, one that is extremely difficult to achieve in gas-liquid chromatography without the help of chemisorptive additives.

Liquid-modified silica gel columns are being tested for possible use in routine analysis of light hydrocarbons. In this application, the amount of polar liquid is extremely critical, and exact column duplications are difficult to attain. This difficulty may be due to variations in the particle size make up in the silica gel containers, the settling out of fines, and the variation of silica gel activity in different production lots. Experimentally, as the average particle size is reduced, appreciably more of the polar liquid phase is required to achieve similar separations.

Multiple auto exhaust samples have been analyzed continuously over 8-hour periods with no adverse effects other than increased base line drift. Continuous 24-hour sampling could adversely affect the column because of an additive effect of the strongly adsorbed polar constituents from the sample.

Water was introduced into the carrier gas with a water diffusion cell to test the effect of water upon the liquid-modified silica gel. As might be expected, the water caused a shift in the relative retention volume values. When the diffusion

cell was removed from the system, the values were restored, an indication that the water did not displace the liquid phase.

Application

The C_1 to C_6 alkanes, acetylene, and benzene represent most of the nonreactive hydrocarbons in photochemical reactions of hydrocarbon and oxides of nitrogen. A gas chromatograph can detect all of these hydrocarbons in a moderately polluted atmosphere (Altshuller and Bellar, 1963). If the values obtained with a gas chromatograph were used in conjunction with those collected by a total hydrocarbon analyzer, one could estimate the total number of reactive species present in a polluted atmosphere. The subtractive methods now used with the total hydrocarbon analyzer are not efficient at ambient air levels. Another use for the system described is an automatic analysis for ethylene in investigations of plant damage. This analysis could be accomplished easily since the ethylene peak is completely resolved from adjacent peaks and is easily detected in the fractional parts per million range.

Perhaps the most significant advantage of gas-solid chromatography over gas-liquid chromatography is the complete absence of the background signal caused by substrate bleed. With electrometer settings above 10^{-11} amp., the signal can be electronically eliminated if all of the operating parameters remain constant. Electrometer settings below 10^{-11} amp. are generally required when individual components in the samples are in the fractional parts per million range or below. Liquid phases and liquid-modified alumina columns commonly used for light hydrocarbon analysis have very high vapor pressure even at reduced temperatures. With electrometer settings in the range 10^{-11} and 10^{-12} amp. the substrate bleed from these columns produces a badly fluctuating base line with random noise. Electrometer settings around 10^{-14} amp. have been reported (Prescott and Wise, 1965) for gas-solid systems. Of course, such a system would require scrupulously cleaned carrier gas, hydrogen, and air in addition to well conditioned columns and plumbing. Electrometer settings in the 10^{-14} amp. range would produce a system from 100 to 1000 times more sensitive (on a mole per second detected basis) than a conventional gas-liquid system. Such sensitivities would be valuable for detection and monitoring of air pollution.

Acknowledgment

The authors are indebted to W. R. Grace & Co., Davison Chemical Division, Baltimore, Md., for providing samples of their silica gels for this work.

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Analysis of the Oxidant in Photooxidation Reactions

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■ A number of methods for determining the identity and concentration of the oxidants produced photochemically in model systems are applied to atmospheric sampling. The Griess-Ilosvay and neutral potassium iodide reagents are evaluated. A novel molybdate-catalyzed potassium iodide reagent and a modification of the ferrous thiocyanate method are presented. The titanium (IV)-hydrogen peroxide complex as a tool in peroxide analysis has high specificity but relatively low sensitivity. The recently published Hauser and Bradley ozone determination is not absolutely specific for ozone. The selectivity and sensitivity of the Mast microcoulometer and the Mark IV ultraviolet photometer are included. The effects of the following variables are considered: spectral characteristics of the reagent blends and the colored species in question; temperature; order of addition, color stability, and rate of color formation; reagent concentrations; hydrogen ion concentration (pH); and various determinate errors. Calibration curves, molar absorptivities, and interferences are presented in detail.

Oxidants are routinely reported as one of the components in photochemical-type air pollution. Phytotoxicant-type plant damage is ascribed to the action of ozone or other compounds with peroxidic linkage. These oxidants are normally measured either manually or instrumentally by use of solutions containing potassium iodide. However, oxidants react with these potassium iodide solutions at widely varying rates; hence the numbers indicating the quantity of total "oxidant" in a given sample may be misleading.

Possible oxidant products may include ozone, hydrogen peroxide, acyl peroxides, alkyl hydroperoxides, peracids, peroxyacyl nitrates, and nitrogen oxides. Some of these react very quickly with neutral potassium iodide solution and thus would probably be detected by the Mast instrument. Others react at a moderate rate, and still others may react with the reagent for many hours before completion of color development.

This paper evaluates a number of oxidant measurements and shows how they may be used effectively to help differentiate among the various types of atmospheric pollutants.

Experimental

Reagents. Highest quality reagent-grade chemicals were used.

Titanium-Sulfuric Acid Solution. This reagent is similar to that cited by Pobiner (1961), with some modification. A mixture of 4.6 grams of basic titanium sulfate (TiOSO_4) and 20 grams of ammonium sulfate was heated carefully in a beaker containing 100 ml. of concentrated sulfuric acid until practically all the solids had dissolved. The solution was then cooled, poured into 350 ml. of distilled water with stirring, and diluted volumetrically to 500 ml. Turbidity may be removed from the solution by suction filtration through very fine sintered glass.

Modified Griess-Ilosvay Reagent (Saltzman, 1954). Five grams of sulfanilic acid was dissolved in an aqueous solution containing 140 ml. of glacial acetic acid and 20 ml. of 0.1% *N*-(1-naphthyl)ethylenediamine dihydrochloride. The resultant mixture was then diluted to 1 liter with distilled water.

Ferrous Thiocyanate Reagent. One-tenth gram of ferrous ammonium sulfate and 1.0 ml. of 6*N* sulfuric acid were added to 200 ml. of water. In a separate container, 50 grams of ammonium thiocyanate was dissolved in water and diluted to 100 ml. This reagent was stored in a dark place to retard decomposition.

Titanium-8-Quinolinol Reagent (Cohen and Purcell, 1967). A novel method incorporates a 0.1% 8-quinolinol in chloroform reagent, a 5% sodium acetate buffer, and a titanium solution consisting of a 1 to 50 dilution of the titanium sulfate reagent described earlier.

Potassium Iodide Reagent (Brode, 1901; Kolthoff, 1951; Savage, 1951; Saltzman and Gilbert, 1959). The neutral buffered reagent consisted of 13.61 grams of potassium dihydrogen phosphate, 14.20 grams of anhydrous dibasic sodium phosphate (0.1*M*), and 10.0 grams of potassium iodide, diluted to 1 liter with distilled water.

The ammonium molybdate solution was prepared by diluting 2.8 ml. of concentrated sulfuric acid and 0.124 gram of ammonium molybdate to 100 ml. with water. These solutions were kept in separate containers.

The concentration of oxidant was sampled with the neutral potassium iodide solution. The effect of the molybdate catalyst was observed by adding 0.5 ml. (or 1.0 ml.) of it to 5 ml. (or 10 ml.) of KI reagent after sampling.

1,2-Di-(4-pyridyl)ethylene (DPE) (Hauser and Bradley, 1966). The method of Hauser and Bradley is a specific spectrophotometric determination of atmospheric concentrations of ozone. The reagent used for the selective ozonolysis is a 0.5% solution of DPE in glacial acetic acid.

Chemicals. Ozone was prepared by metering ultrapure tank air through a generator consisting of several 4-watt

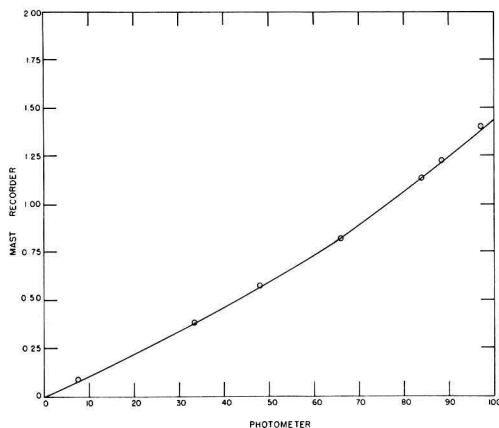


Figure 1. Ozone photometer response vs. Mast recorder

mercury vapor lamps. Peroxyacetyl nitrate (PAN) was obtained from the University of California Air Pollution Laboratories. Peroxypropionyl nitrate (PPN) was prepared by the photooxidation of low concentrations of 1-butene in the presence of nitrogen dioxide (Stephens *et al.*, 1965). Hydrogen peroxide and nitrogen dioxide were obtained from commercial sources. Ethyl hydroperoxide and *n*-butyl hydroperoxide were synthesized by literature procedures (Minkoff, 1954; Mosher and Wurster, 1956; Williams and Mosher, 1954).

Results and Discussion

Potassium Iodide Reagents. Only a few micrograms of active oxygen were required for KI colorimetry. In each case, the oxidant was transferred by pipet (for liquid-phase samples) or sampled by means of a fritted bubbler (for vapor-phase analysis) into 10 ml. of neutral potassium iodide. The flow rates were restricted to 0.5 to 1 liter per minute.

When the catalyzed KI technique was desirable, the ammonium molybdate solution (1 ml.) was mixed with the neutral KI reagent (10 ml.) immediately after sampling. The iodine complex liberated by the oxidant was measured spectrophotometrically at 352 $m\mu$.

With neutral KI, peracid and ozone give rise to an immediate absorbance maximum. Peroxide compounds are responsible for a much slower liberation of iodine. With molybdate-catalyzed KI, hydrogen peroxide exhibits an instantaneous absorption maximum. The alkyl and acyl peroxides, however, exhibit very slow color development.

The molar absorptivities of the various oxidants are listed in Table I, under the appropriate reagents. Whenever a particular oxidant-reagent combination gives rise to a slowly developed color, the molar absorptivity is derived from the maximum absorbance reading. The wide range of these absorptivity values is interesting and further investigation to elucidate the mechanism of the colorimetric reactions involved would be valuable.

Mark IV Ozone Photometer. The ultraviolet channel for the Mark IV atmosphere analyzer (Beckman Instruments, Inc.) measures ozone directly by absorption spectroscopy. The source lamp contains mercury vapor, which emits 80% of its energy at the strong 2536.5- \AA . line. The sample cell includes three mirrors so arranged that the ultraviolet beam passes the length of the cell eight times before going to the sample phototube. This arrangement provides an absorption path length of 21 feet.

The normal rate of flow of samples through the instrument is 12 cubic feet per hour. The instrument is repeatedly flushed and actually zeroed with a flow of purified tank air.

Ozone is determined quantitatively (in the range of 0 to 3 p.p.m.) in the presence of hydrocarbon interferences by observing the decrease in the indicator meter reading after inserting into the sampling system the scrubber column containing finely crushed natural rubber. The indicator reading after allowance for mercury vapor and ozone is attributable to acetone, benzene, toluene, xylene, and the like.

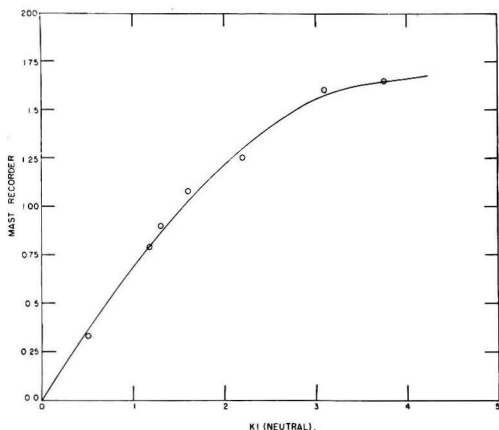


Figure 2. Mast response to ozone vs. neutral KI

Figure 1 is a plot of photometer meter readings vs. Mast recorder readings for various vapor concentrations of ozone in air. Unlike the calibration curve in the Mark IV manual, the response is not quite linear in the 0- to 3-p.p.m. range.

Mast Ozone Meter. The Mast "ozone-meter" employs microcoulometry to measure the total oxidant in the atmosphere (Wartburg *et al.*, 1964). This instrument is particularly sensitive to the reaction of ozone with potassium iodide-potassium bromide reagent. The iodine formed by the oxidation reaction is continuously reduced by an externally applied potential of about 0.25 volt. The current required is a measure of the oxidizing capacity of the sample. If ozone is the only oxidant present, this current is a linear function of the ozone concentration and the flow rate of sample through the cell. Calibration of the Mast instrument with various concentrations of ozone stored in conditioned bags fabricated of fluorinated ethylene-propylene copolymer (FEP Teflon, Du Pont), indicated that the scale provided on the ammeter gave low readings. A plot of Mast recorder readings against parts per million of ozone (as determined by manual neutral KI meas-

urements) demonstrates that the ratio of KI to Mast values is 1.4 to 1.5 over the 0- to 2-p.p.m. range. In the 2- to 4-p.p.m. range, this ratio increases to 1.8 (Figure 2).

Iodometric Titration of Peroxy Compounds. The purity of aqueous stock solutions of hydrogen peroxide and the organic peroxides was determined by titration iodometry (Kolthoff and Sandell, 1955; Ricciuti *et al.*, 1955). Approximately 1 gram of commercial hydrogen peroxide solution (about 30% by weight) was placed in a stoppered vial and accurately weighed on an analytical balance. The sample was then transferred to a 500-ml. volumetric flask and diluted to the mark with distilled water (solution A). Although hydrogen peroxide solutions are unstable over long periods of time, small amounts of acetanilide or urea can serve as preservatives.

The analytical procedure consisted of pipetting a 10-ml. aliquot into a glass-stoppered Erlenmeyer flask, and adding 2 ml. of 6N sulfuric acid, 1.5 grams of potassium iodide, 2 ml. of a solution containing 0.124 gram of ammonium molybdate plus 2.8 ml. of concentrated sulfuric acid per 100 ml. of water, and 25 ml. of water. This mixture was titrated, by use of a microburet and starch indicator, with sodium thiosulfate solution (~0.1N), which itself was analyzed with primary standard potassium iodate solution.

The commercial hydrogen peroxide solution was found to be of 30.7% purity (specific gravity 1.108). Solution A was therefore equivalent to 612 μg . of H_2O_2 per ml. and was further diluted volumetrically 1 to 10 and 1 to 50 to prepare solutions for calibrating the colorimetric reagents.

Equimolar concentrations of peracetic acid, ethyl hydroperoxide, acetyl peroxide, *n*-butyl hydroperoxide, and *tert*-butyl hydroperoxide were similarly prepared and analyzed by titration with standard thiosulfate solution. The weighed sample in each case was transferred to a glass-stoppered

Table I. Molar Absorptivities

	KI		$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (NH_4SCN)	Ti(IV) [8-OQ]	DPE	NO_2 Equiv.
	Neutral	Catalyzed				
Ozone	24,200 ^a	27,800	28,700	—	26,000	38,200 ^a
Peracetic acid	26,200	28,800	55,300	—	—	—
H_2O_2	24,000	27,000	33,500	770 [3,000]	2,900(1) 4,400(v)	—
Acetyl peroxide	24,000	32,600	19,300	—	—	—
Ethyl hydroperoxide	20,200	22,600	43,800	—	—	—
<i>n</i> -Butyl hydroperoxide	43,300	47,700	67,400	—	—	—
<i>tert</i> -Butyl hydroperoxide	—	—	57,300	730	—	—
NO_2	2,400	—	5,000	—	—	31,400
PAN	—	—	9,200 (est.)	—	—	—
PPN	—	—	—	—	—	—

^a Hendricks and Larsen (1966).

250-ml. iodine flask; then the potassium iodide, sulfuric acid, and ammonium molybdate catalyst were added and the flask was flushed quickly with nitrogen. After sufficient time for the peroxide compounds to react completely, water was added and the liberated triiodide complex was titrated.

Reaction of Titanium Reagent with Peroxides. A solution containing 1 gram, weighed to the nearest 0.1 mg. of standardized hydrogen peroxide in 500 ml. of distilled water was diluted 1 to 10 with water, and aliquots were pipetted into 10-ml. volumetric flasks: 0 (blank), 0.5, 1, 2, and 3 ml. To each were added 1 ml. of titanium reagent and 2.5 ml. of 1 to 1 sulfuric acid. The solutions in the flasks were heated in a water bath at 60°C. for 10 minutes. After cooling and diluting to volume, the spectrum of each was scanned against that of the blank with a Cary Model 14. The absorption maximum is about 407 m μ for the titanium-peroxysulfate complex.

Volume parts per million concentrations of hydrogen peroxide were prepared by injecting microliter quantities of liquid "30%" H₂O₂ into a metered stream of dry air while filling a Teflon FEP bag to a predetermined volume. Contents of the bag were analyzed by sampling a measured quantity of the vapor mixture through a fritted bubbler containing 10 ml. of titanium sulfate reagent. The resulting absorbance at 407 m μ is a measure of the hydrogen peroxide concentration in the bag. For the more dilute mixtures, 10-cm. absorption cells were used to achieve the necessary increase in sensitivity. Analyses of various hydroperoxides with the titanium complex are reported in the literature (Pobiner, 1961; Wolfe, 1962). The hydroperoxide is converted quantitatively by acid hydrolysis to hydrogen peroxide, which is determined as the peroxy-titanium complex. Although Satterfield and Bonnel (1955) originally reported that the absorptivity of *tert*-butyl hydroperoxide was 0.002 times that of hydrogen peroxide, the 10 minutes of heat resulted in equivalent molar extinction coefficients. Even without the hydrolysis step, the *tert*-butyl hydroperoxide and titanium reagent gave increasing absorbance readings upon standing at room temperature.

Equimolar dilutions of ethyl and *n*-butyl hydroperoxide did not respond to the titanium reagent. This result can be related to differences in the decomposition products of primary hydroperoxides from those of secondary and tertiary hydroperoxides (Mosher and Wurster, 1955). The *tert*-butyl hydroperoxide probably decomposes by alkyl-oxygen cleavage; the *n*-alkyl hydroperoxides undergo cleavage at the O—O bond (Hoare and Pearson, 1964).

Another method for determining microgram quantities of hydrogen peroxide was recently developed in our laboratories. The analytical procedure uses the colored complex obtained upon extraction of titanium-H₂O₂ mixtures with 8-quinolinol in chloroform. The method is very specific; Figure 3 shows that its sensitivity is at least 4 times greater than that of the titanous sulfate method. An additional advantage in the procedure is that the colored species is soluble in a relatively volatile organic solvent. With evaporation techniques, the

sensitivity of the method could be increased 10-fold by use of microcells for the absorbance measurements.

Response of Ferrous Thiocyanate Reagent to Oxidants. Attempts at using the Egerton thiocyanate method (Egerton *et al.*, 1954) and the Todd (1955) modification did not achieve the desired sensitivity level for peroxides. The short shelf life of the mixed reagent and the instability of the color development upon treatment with peroxides also suggested the possibility of further modification.

A vapor dilution of peroxide in air was bubbled through the mixed ferrous thiocyanate reagent and the absorbance was read at 480 m μ *vs.* that of the blank reagent. When more ammonium thiocyanate solution, equivalent in concentration to that already present in the reagent, was added to both the sample and the blank, the absorbance doubled. After much experimentation, it was decided to keep the two reagent components separate until after sampling into the ferrous ammonium sulfate solution. Then the color development step was effected with a 2-ml. aliquot of a 50% (weight by volume) aqueous solution of ammonium thiocyanate.

A sample of ozone in air (3.36 p.p.m. as measured by neutral potassium iodide) was bubbled through ferrous ammonium sulfate solution, and 2 ml. of ammonium thiocyanate was added to both the sample and the blank. The calculated molar extinction coefficient was 28,700. The molar extinction coefficients, ϵ_m , for hydrogen peroxide, ethyl hydroperoxide, peracetic acid, *tert*-butyl hydroperoxide, and *n*-butyl hydroperoxide were 33,500, 43,800, 55,300, 57,300, and 67,400, respectively. Plots of concentration of peroxide (micrograms of O₂⁻ per milliliter) *vs.* absorbance indicated Beer's law correlation for each oxidant studied (Figure 4).

In the search for a specific colorimetric method for ozone, difficulties were encountered with the nitrogen dioxide equivalent method of Saltzman in environments where the nitrogen dioxide concentration was somewhat higher than the ozone concentration. Small changes in NO₂ levels could be misinterpreted as ozone responses; moreover, PAN compounds give a positive interference to the colorimetry.

Even the Hauser DPE reagent was not specific enough for some of our uses. Figure 5 shows that a positive interference arises from hydrogen peroxide. A 15% average molar response was observed in liquid-phase studies; a 30% response was found by sampling vapor mixtures.

Application of Methods to Model Systems. Attempts to evaluate the reactivity of photochemical smog by use of existing data on the rate of formation or yield of oxidant may be misleading. The term "oxidant" is very comprehensive, including ozone, nitrogen oxides, various peroxy compounds, and free radicals. Because of the differences in response of the various so-called "standard" methods to the menagerie of oxidants, it is extremely difficult to relate reported values to photochemical reactivities (Altshuler, 1965).

Claims of specificity for determination of ozone, peroxide, and nitrogen oxides require some scrutiny. The more specific

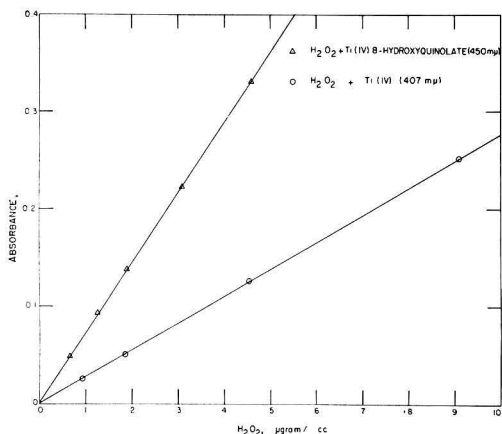


Figure 3. Comparison of titanium sulfate and Ti(IV)-8-quinolinol methods

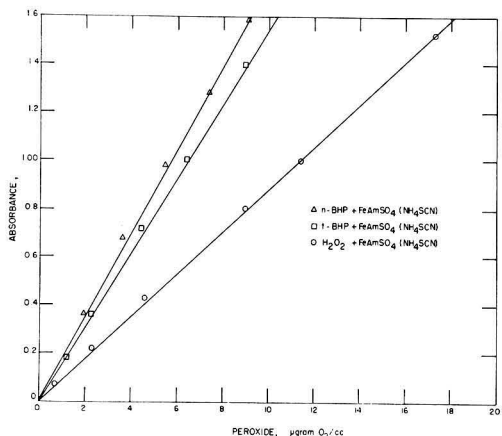


Figure 4. Beer's law correlations using ferrous thiocyanate reagent

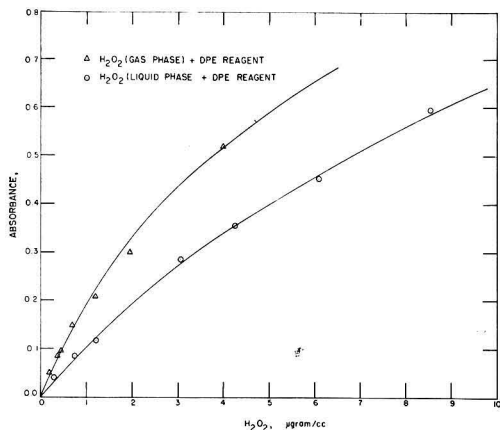


Figure 5. Hydrogen peroxide interference using DPE reagent

methods, such as infrared and ultraviolet measurements or the hydrogen peroxide-titanium colorimetric determination, are not nearly as sensitive as the less discriminating redox colorimetry. For example, the rubber-cracking technique has long been thought absolutely specific for ozone analysis. Yet, infrared evidence given by Schuck and Doyle (1959) indicates that the irradiated ethylene- NO_x system produces higher ozone concentrations than the other olefin- NO_x systems studied. On the other hand, rubber-cracking data on these same systems show the ethylene- NO_x mixture as one of the poorest ozone producers (Haagen-Smit and Fox, 1956). Furthermore, plant damage due to ozone is undetectable for the ethylene- NO_x mixtures, while other olefin-nitrogen oxide mixtures produce a phytotoxicant (Altshuller *et al.*, 1967; Heck, 1964).

In explanation of these results, recent work in our laboratories has shown that the irradiation of several simple model systems gives evidence of three or more distinct oxidants. Photolysis of formaldehyde in air leads to the production of hydrogen peroxide as determined by the titanium sulfate and catalyzed potassium iodide methods. Irradiations of ethylene-nitrogen oxide mixtures indicate that the oxidant is probably ozone, plus hydrogen peroxide and a slow-reacting oxidant such as an organic hydroperoxide. Irradiation of propionaldehyde-air and acetaldehyde-air mixtures reveals the presence of ethyl hydroperoxide and methyl hydroperoxide, respectively. In this work, gas chromatography can be misleading, especially when one finds that hydroperoxides can catalytically or thermally decompose to the corresponding aldehyde and/or alcohol (Altshuller *et al.*, 1966), both of which are likely secondary products of aldehyde photolysis.

Bufalini and Altshuller (1965) reported no slow oxidant formation with the 1-hexene-ozone system. Conversely, Saltzman and Gilbert (1959), in their investigation of the ozone-hexene reaction, found an oxidant which liberated iodine slowly from KI reagent.

Application to Atmospheric Sampling. The ferrous ammonium sulfate-ammonium thiocyanate colorimetric method for oxidant determination offers an excellent tool for field or monitoring station work. The oxidation potential for the ferrous-ferric system is more negative (-0.78 volt) than that for iodide (-0.59 volt) and therefore air oxidation interferes with it much less (Wolfe, 1962). The volatility problem found with the I_2 -KI₃ oxidant method is also absent. When 100 liters of tank air were sampled through the ferrous ammonium sulfate reagent, the subsequent color development step showed negligible absorbance.

The ozone photometer, with its high-flow-rate requirement, also applies well to atmospheric air sampling. Its fast response time, ease of handling, low interference level, and high specificity could make it a useful tool for correlating total oxidant data with atmospheric ozone concentrations. The instrument is portable and extremely rugged. The only drawbacks are cost and availability.

Table II. Analytical Tools for Oxidant Determination

	KI		MG ^a	Fe(NH ₄) ₂ (SO ₄) ₂ (NH ₄ SCN) Ti(IV)			Mast	UV Photometer	DPE
	Neutral	Catalyzed		NO ₂ Equiv.	Ti(IV)				
Ozone	A	A	D(10%)	A	A	N	E	E	A
Peracetic acid	A	A	—	N	A	N	—	N	N
H ₂ O ₂	B	A	—	N	A	A	D	N	D
Acetyl peroxide	B	B	—	N	B	N	N	N	—
Ethyl hydroperoxide	B	B	—	N	A	N	—	N	—
<i>n</i> -Butyl hydroperoxide	B	B	—	N	A	N	—	N	D
<i>tert</i> -Butyl hydroperoxide	B	B	—	N	A	C	—	—	D
NO ₂	D(10%)	D	A	—	B	N	D(10%)	D(3%)	N
PAN	D	D	D	D	B	N	N	N	N
PPN	D	D	D	DB	B	—	D	N	—

A = immediate stable color.
 B = slow color development.
 C = color development after $\Delta w H^+$.
 D = positive interference.
 E = good response; see calibration chart.
 N = no response (or negligible).

^a Modified Griess-Ilosvay reagent (Saltzman, 1954).

Conclusions

The molar extinction coefficient of the ozone-ferrous thiocyanate color development is second only to that of the nitrogen dioxide equivalent method (Table I). The molar absorptivity of a particular oxidant is always higher with catalyzed KI than with neutral KI. Ferrous thiocyanate, with its over-all superior sensitivity to oxidant, along with its lack of specificity, would be a good choice for total oxidant measurements. The titanium methods have high specificity but relatively low sensitivity. The Hauser DPE reagent is not absolutely specific for ozone when the oxidant mixture contains hydrogen peroxide in the parts per million concentration range. Preliminary investigations with *n*- and *tert*-butyl hydroperoxides indicated a similar interference with the DPE reagent.

Table II demonstrates use of the combination of reagents and instrumental methods to determine and distinguish among the various oxidant materials. It indicates that the ultraviolet photometer is specific for ozone. The nitrogen dioxide equivalent method, while rather specific, is interfered with by NO₂ and PAN compounds. Acetyl peroxide, NO₂, and PAN compounds produce slow color development with ferrous thiocyanate reagent, each at its own specific rate. Neutral KI shows immediate response with ozone and peracetic acid and slow color development with other peroxides. Molybdate-catalyzed KI gives immediate response with H₂O₂ along with O₃ and peracid. Titanium reagent is specific for hydrogen peroxide and for any peroxide that can liberate H₂O₂ via acid hydrolysis.

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NEW PRODUCTS DIGEST

Density Cell for Fluids or Slurries

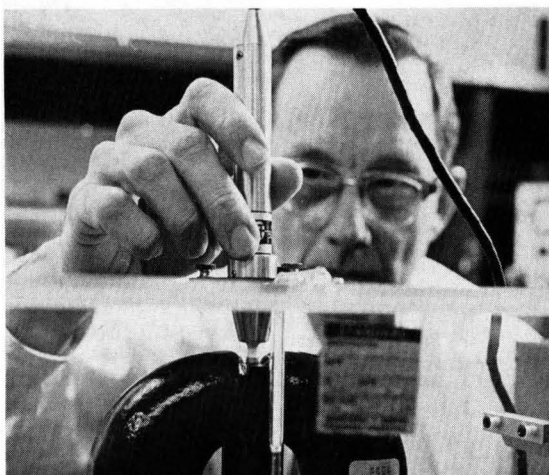
Model CL-10TY series Dynatrol density cell utilizes a new design principle for the measurement or control of density or specific gravity. A positive active electrical output signal varies in response to the density or specific gravity of the process media, whether a liquid or a slurry. The density cell is not sensitive to changes in ambient temperature, viscosity, pressure, or flow velocity. The cell is corrosion-resistant and pressure-rated for 1000 p.s.i.g. Automation Products, Inc. 61

Slurry Pump

A new 2-inch, self-priming slurry pump is capable of handling 1½-inch spherical solids and can operate at suction lifts to 25 feet. A quick-twist "L" screw provides access to the suction inlet check valve and impeller eye, while four hand-operated knobs allow removal of the cover plate for complete pump inspection and servicing; neither of these actions requires tools. As part of the standard design, the pump has a removable wearplate and removable volute to assure inexpensive factory performance restoration. ITT Marlow. 62

Filtration Process for Emulsions

A new filtration process eliminates the need to replace emulsions used as lubricant-coolants in rolling aluminum and magnesium. The process involves addition of two chemicals and filtration through diatomaceous earth, permitting indefinite reuse of oil-in-water emulsions. During a three-year field test of the process, the emulsion required only periodic replenishment to cover normal losses. Other advantages include a lower yearly emulsion expense, a reduction in labor costs for cleaning mills and tanks, a higher production rate brought about by less equipment down-time and more consistent performance. Maintenance is effected with simple, readily available laboratory apparatus. Dow Chemical Co. 63



First nationwide, all-industry metrology service established

Maintenance, repair, and calibration services are now available for users of electronic test instruments. The service, which is available from Honeywell, Inc., has a three-fold objective: calibration of measurement standards, repair and maintenance of electrical and electronic test instruments, and providing other instrument manufacturers with factory-authorized warranty service. Here, a metrologist uses a special magnet, calibrated by the National Bureau of Standards, to determine field intensities of other magnetic devices used by government and industry for a variety of applications. 65

Acid Analyzer

A continuous analyzer for direct measurement of the concentration of hydrochloric, sulfuric, or nitric acid in a process stream or bath utilizes an amperometric-type measuring cell which has been field proven in other analytical systems. Measurement and control over a wide range of acid concentrations, temperatures, and sample compositions is possible with this enclosed free-standing floor cubicle of all fiberglass construction. A 12-inch circular chart

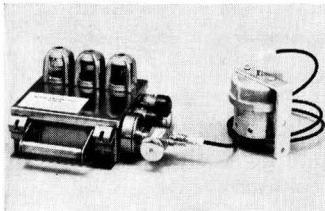
recorder or 5¼-inch indicator is included for local indication of acid concentration and either pneumatic or electronic transmission to central control facilities is available, or local pneumatic control may be included in the analyzer housing for complete local control of acid concentrations. The system is normally supplied complete with sample pump and filters. Package systems as well as individually-designed systems are available. Fischer & Porter Co. 64

High-Efficiency Dust Collector

A high efficiency dust collector featuring a top air entry and a high rate of air flow (12.2 c.f.m.) per square foot of cloth has proved especially useful as a reclamation device for plastic resins, retrieving large and small particles from the air in the same ratio that they are fed into the collector inlet. Field tests have shown operating efficiencies of 99.8%, removal of particles as small as 20 μ , flow rates of about 10 c.f.m. per square foot of cloth, and small pressure differentials in the range of 0.5 to 1.5 inches water gage. Hydromation Engineering Co. 66

Methane Monitoring System

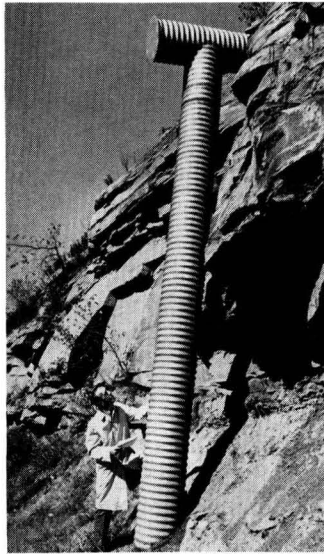
A methane monitoring system featuring a practically indestructible remote (up to 100 feet) inlet probe and miniaturized circuitry that operates from a 4-volt power source (a.c., d.c., or battery) has been certified by the Bureau of Mines for use in gassy coal mines. The system, M-S-A Methane Monitoring System Model IV, utilizes a very small, catalyzed ceramic bead supported on a coiled



filament, allowing operation at half the temperature required by conventional platinum filaments. The device uses very little power, has an exceptionally long life, and almost no zero drift. A series of signal lights warns of dangerous methane concentrations. Also available: relays to shut down the coal-cutting machine when methane concentration exceeds 2%, a meter showing concentrations from 0 to 4%, and multiple inlet probes. Mine Safety Appliance Co. 67

Personnel Radiation Monitor

A personnel radiation monitor gives a distinctive chirp when beta or gamma radiation is present. The 4-ounce unit operates on ordinary 9-volt carbon batteries. It uses standard parts and, when necessary, is readily repaired. Electro-Neutronics, Inc. 68



MF-1 Stainless Steel for Culvert Applications

Comparison tests on culverts of carbon steel, galvanized steel, aluminum, and stainless steel types MF-1, 201, and 363 revealed that in severely corrosive or abrasive environments, newly developed MF-1 provides the best combination of functional resistance, structural integrity, long service life, and economy. Extrapolation of the results of corrosion on MF-1 samples gives an expected product life of more than 100 years. A low-priced grade of stainless steel originally developed for automotive mufflers, MF-1 is now used in water tanks, transformer cases, cargo containers, and agricultural equipment. Allegheny Ludlum Steel Corp. 69

Teflon Gas Sampling Pump

The Komhyr Teflon gas sampling pump transfers chemically active gases without contaminating or destroying them because gas-contacting parts, which are Teflon reinforced with 15% glass fiber, require no lubrication. Pumping speed is approximately 200 ml./min.; pressure or suction equivalent to a 3-inch column of mercury is developed under normal operating conditions; and the pump performs satisfactorily at atmospheric pressures from sea level to 2 millibars. The pump is suitable for battery operation (current drain is only 250 milliamperes). Science Pump Corp. 70

Oxygen Demand Index Colorimeter

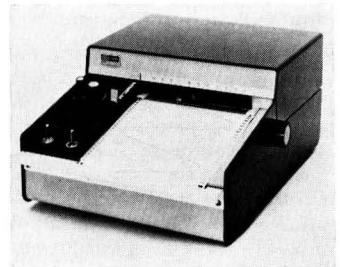
Colorimetric determination of waste strength takes only 35 minutes using this direct-reading, a.c.-operated colorimeter precalibrated for ODI calculation. Following dichromate-sulfuric acid oxidation in a boiling water bath for 20 minutes, the reduction of yellow chromate ion to green chromic ion is measured colorimetrically. All necessary apparatus and reagents are included. Multiple determinations may be conducted simultaneously. Hach Chemical Co. 71

Temperature Gage for Aerospace Use

An aerospace-quality Bourdon-Helix temperature gage, Model G-3531, is based on the pressure-temperature characteristics of two-phase (liquid/gas) systems. As the temperature of the remote probe changes, the change in vapor tension of the fluid sealed in the probe is transmitted to a Bourdon-Helix indicator which shows the temperature in degrees Fahrenheit. Accurate within +5% of full scale from -20° to +200° F., the unit is highly resistant to extremes of shock, vibration, and over-temperature. Glassco Instrument Co. 72

Strip Chart Recorders

Series G-1000 5-inch strip chart recorders are available in two models—the G-1010 multiple span unit for general laboratory work, and the G-1110 single span unit for OEM applications. Special versions equipped with filter networks for gas chromatography, spectrometry, radiation detection, and so



on are available. Sensitivity of the recorder is 0.1% of the 5-inch span; accuracy is 0.25% or better; and pen response is 0.35 second, full scale. Four chart speeds (eight speeds available upon request) are provided. Solid state design and electronically-regulated reference circuits afford reliable operation for long periods. Varian Associates. 73

Dual DO Output/Temperature Recorder

A portable dual-purpose instrument for recording output of a DO electrode and/or temperature has been developed for dissolved oxygen applications. DO/TEMP Model 192 is a weatherproof recorder which provides a permanent independent record of both parameters on a single strip-chart. Adjustable



from 15 to 300 microamperes (by means of a potentiometer), the DO channel accommodates most galvanic DO electrodes and can be accurately reset without actual calibration. The temperature channel has a range of 0° to 40° C. A battery powered regulated d.c. motor maintains chart speed accuracy of $\pm 0.5\%$. Rustrak Instrument Co. 74

Sludge Conditioner

ST-260 sludge conditioner conditions sewage sludges in preparation for vacuum filtration, aids in concentration or air flotation of sewage sludges, and increases removal of suspended solids in both primary settling tanks and final effluent clarifiers. The flake-like, cationic polyelectrolyte is readily prepared in solutions for laboratory or plant use, and is noncorrosive to ferrous metals. Calgon Corp. 75

Potentiated Silylating Agent

A chemical reagent for preparing volatile and thermally stable derivatives of many high-boiling or thermally unstable compounds such as amino acids, amides, organic acids, phenols (even highly hindered), other hydroxyl or polyhydroxyl compounds such as glycols, sugars, and other carbohydrates, is available. Called Tri-Sil/BSA, the reagent is offered in 1 ml. glass ampules or 25 ml. elastomer capped serum vials. Pierce Chemical Co. 76

Filter System for Corrosive Solutions

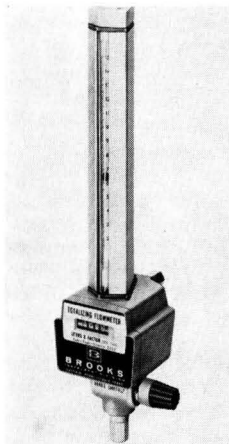
A noncontaminating filter system has been developed for all corrosive or abrasive solutions, including electroless nickel and copper to 200° F. Constructed of polyvinylidenechloride, the pump has no bearings, no seals, and no wearing parts, and is virtually maintenance-free. Open pumping capacity is 300 g.p.h. and pressure developed at zero flow is 11 p.s.i. Sethco Manufacturing Corp. 77

Dew-Point Tester

A new gas dew-point tester allows operation at actual flowing pressure, eliminating the necessity of reducing gas pressure to atmospheric pressure. Model A2 is rated at 3000 p.s.i. working pressure, and Model B at 1000 p.s.i. working pressure. Safe observation into the pressure chamber is provided by a mirror. The testers are specifically designed for field use, but are equally convenient in the laboratory. Chandler Engineering Co. 78

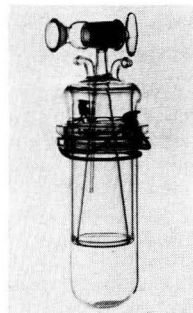
Totalizing Flowmeter for Gas

A totalizing gas service flowmeter that also gives instantaneous flow rate is a unique blend of rotameter and 5-digit totalizer. Designed for use with any non-corrosive gas, Brooks totalizing flowmeter is available in 65 mm. and 150 mm. scale lengths and flow ranges up to 20 liters per minute. Maximum temperature rating is 150° F.; maximum pressure is 100 p.s.i. at 70° F.; and minimum pressure is 30 p.s.i. at 70° F. Reproducibility is $\pm 0.5\%$ of instantaneous reading. Brooks Instrument Division. 79



Sublimator for Special Compounds

The Nester/Faust McCarter sublimator is designed for rapid sublimation of high-boiling or heat-sensitive compounds at normal pressures. Constructed of heat-resistant borosilicate glass with a greaseless O-ring joint and a lapped vacuum stopcock, the sublimator is ideal for high-vacuum operation. The pure sublimate forms inside the



inverted conical condenser. After condensation, the large O-ring opening permits easy removal of the bottom outside shell and the smooth inside taper permits fast recovery of the purified crystals. Available in 10-, 50-, and 100-gram capacities, the sublimator comes supplied with a ball joint adapter and vacuum hose connection. Nester/Faust Mfg. Corp. 80

Rotary Drum Screen for Water Intake

A low-cost rotary drum screen for water intake for plant cooling or emergency generating systems supplies 1000 to 3000 gallons of screened water per minute. Debris that collects on the screen is removed on the down-stream side by four spray nozzles. All operating parts are above the water line for easy installation, operation, and maintenance. Rex Chainbelt, Inc. 81

Water Treatment Kit

A water treatment kit designed for use with private water systems contains complete instructions as well as all necessary tubing, strainers, and fittings, for reducing undesirable odors, minerals, disease-causing bacteria, and color in well water. After treatment by laundry bleach supplied through a solution feeder, the water is filtered through a paper or carbon element contained in a Cylolac case in the storage tank discharge line. Mec-O-Matic, Inc. 82

Deposit Inhibitor

CL-77 deposit inhibitor retards the formation of carbonate deposits of calcium and iron, and the sulfate scales of calcium, barium, and strontium. Designed for use in heat exchangers, condensers, pumps, tanks, transmission pipe lines, and other nonpotable water applications involving high temperatures or long retention periods, the liquid remains stable to 400° F. Calgon Corp.

83

High-Speed Flexible Coupling

Series 61 flexible couplings for high-speed, high-torque applications are designed for maximum strength and flexibility for installations that demand low weight at ultra-high speeds. The new couplings feature hubs and center members of heat-treated alloy steel. They have no backlash or free end float. They accommodate angular and parallel misalignment, need no lubrication, have no wearing parts, and maintain close balance for life. Rex Chain-belt, Inc.

84

Industrial Fabric for Filters

A new fabric is composed of a mat of ultra-thin stainless steel fibers fully impregnated with Teflon resin and combined with glass filament reinforcement. Known as Fibermet, the fabric is used for smog control and manufacturing operations requiring demisters and phase separators. It can withstand tempera-



tures in excess of 500° F. and is corrosion resistant, yet possesses much higher permeability than conventional materials performing similar functions (typical air flow: 60 c.f.m. at 0.3-inch water column per square foot). The fabric has a nominal thickness of 1/8-inch, and tensile strength of 115 pounds per inch of width. Pallflex Products Corp.

85

Ultrasonic Cleaners

A line of separate, matching ultrasonic cleaning tanks and solid state generators designed for precision cleaning of metals, ceramics, glass, and plastics, is available. The tanks have capacities ranging from 1 to 30 gallons with matching, 22 kHz, all solid state, radio-interference-free generators rated from 100 to 4000 watts average output power. High efficiency electrostrictive transducers are permanently attached across the bottom of the stainless-steel tanks. Acoustica Associates, Inc.

86

Spectroscopy Laboratory

A complete spectroscopy laboratory consisting of infrared and ultraviolet spectrophotometers with built-in laboratory recorder is available in a single, compact unit. The system permits spectroscopic analyses in both the 205 to 770 m μ and 2.5 to 14.5 m μ wavelength ranges. A single switch permits recording-i.r. to recording-u.v. capability. Beckman Instruments, Inc.

87

WE SOLVE AIR POLLUTION PROBLEMS

99% removal of corrosive fumes and noxious gases is possible with a Heil fume scrubber. Used in chemical and fertilizer plants . . . in paper and steel mills, Heil scrubbers are corrosion-proof inside and out. Made of solid plastic, Model 730 is 1/3 the weight of steel, 1/10 the weight of ceramic . . . may be easily mounted on a roof. We also design and build corrosion-proof fans, ducts, hoods, tanks and stacks for your complete system.



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NEW LITERATURE DIGEST

Laboratory apparatus catalog. An 81-page catalog describes in detail a line of glass fiber fume hoods, laboratory blowers, glove boxes, tissue culture hoods, carts, Kjeldahl apparatus, fat extractors, and crude fiber apparatus. Included are engineering data on design and construction, full-page illustrations, and listings of accessories. Labconco Corp. 88

Waste treatment system. A bulletin is available on a waste treatment system using the Air-Aqua controlled aeration concept. The system can be used for treating domestic or industrial waste, providing primary settling, secondary treatment, sludge disposal, and effluent polishing. Hinde Engineering Co. 89

Waterproof rubber surfaces. A 24-page color brochure illustrates the use of waterproof rubber surfaces through extensive use of photographs and drawings. Of particular use to architects and specification writers, it covers use of rubber liners in antipollution systems, canals, lagoons, pits, foundations, and reservoirs. Uniroyal, Inc. 90

Chromatographic columns. A 6-page bulletin discusses choosing the proper gas chromatographic column for a particular application. The illustrated bulletin covers partition liquids, solid absorbents, mesh sizes, fittings, and solid supports. Also included are specifications and prices for many of the more than 200 partition and adsorption columns available for immediate delivery. Custom-made columns are also listed. Beckman Instruments, Inc. 91

Flow adaptor for gel filtration columns. A product bulletin illustrates and describes a flow adaptor for quick conversion of a laboratory column from a descending to an ascending system. For ascending chromatography with porous gels, the adaptor minimizes compression of the gel bed and allows for fine control of the flow rate. The adaptor can also be used with automatic recycling chromatography. Pharmacia Fine Chemicals, Inc. 92

Trash rack rakes. A bulletin gives information on trash rack rakes for use in water intakes for public utilities, municipalities, power stations, water treatment plants, and industrial plants where protection from heavy debris is needed. Simply designed units operated by one man, they can be installed in most existing intake structures. The new rakes are positive cleaning, have hydraulic control, and provide for self-dumping into an internally mounted debris hopper. They are available for light, medium, or heavy duty service in fixed, manually propelled, or self-propelled models. Rex Chainbelt, Inc. 93

Sintered metal filters. Four bulletins (10 pages) describe a line of fiber metal filter products with filtration ratings from 0.1 to 200 microns. The bulletins give design and performance data for a wide selection of filter media, fabricated elements, and complete filter units. The products are made of a controlled porosity material formed by sintering aggregates of carefully sized metal fibers. In filtration operations, this material has substantial advantages in flow rate, contaminant holding capacity, and strength, compared with other forms of porous metal. The bulletins list uses where high temperatures and pressures are involved, including applications in the chemical, nuclear, petrochemical, aircraft, pharmaceutical, and food industries. Huyck Metals Co. 94

Metal corrosion. A 102-page booklet describes how sodium chromate and sodium bichromate can prevent corrosion of all common metals in contact with aqueous solutions. With the aid of graphs, tables, and technical data, the booklet tells how chromate corrosion treatment can be low in cost, effective over a wide range of pH, temperatures, and concentrations of dissolved salts, and suitable for both open and closed systems. In open systems, chromates are said to be compatible with chlorination and most algicides; they are not affected by microorganisms in the system. Allied Chemical Corp. 95

Filters for air and gases. A 4-page bulletin gives data on a line of filters that removes oil, water, and solid contaminants from air and gases and that can be used either independently or in conjunction with air-gas dryers. The bulletin describes Reverse Ultipor 2 prefilters used upstream of air/gas dryers and Epocel afterfilters used downstream of adsorbent dryers. Illustrated with photographs and charts, the bulletin includes information on removal ratings, absolute cut-off ratings, flow rates, and pressure drops. A complete guide for selecting and ordering filters and housings is included. Pall Trinity Micro Corp. 96

Field testing with ozone. A 5-page brochure is available on field evaluation of the use of ozone in water and waste treatment. The brochure discusses the advantages of continuous on-site tests compared with batch tests in the laboratory. It covers testing procedures, equipment required, and analyses to be made. Welsbach Corp. 97

Contamination control system. Bacterial contamination of machine coolants can be controlled without special down time. A machine cleaner is added directly to the contaminated coolant, which is then recirculated while the machine remains in production. S. C. Johnson & Son, Inc. 98

Air and water literature index. The first monthly issue of *Subject Index to Current Literature on Air and Water Conservation* has been published. The index covers basic research in air and water pollution control methods; specific pollutants and their sources; control methods mainly related to the oil industry, but including other industries; measurement, sampling, and analysis; effects of pollution on human health, plants, animals, and materials; and legislative and regulatory aspects of pollution control. Each issue will include references to journal articles, reprints, reports, abstracts, and meeting papers. American Petroleum Institute. 99

Pollution Abatement Is More Than Waste Treatment

River Pollution 3: Control. Louis Klein. xv + 484 pages. Butterworths, Inc., Washington, D.C. 20014. 1966. \$20, hard cover. *Edward J. Cleary is executive director and chief engineer of the Ohio River Valley Water Sanitation Commission, Cincinnati, Ohio 45202*

By Edward J. Cleary

Several years ago an acquaintance who sought to familiarize himself in depth with the science and technology of water-pollution control asked me to suggest some appropriate books. I named three, among them *Aspects of River Pollution*, by Louis Klein. This British treatise, initially published in 1956, not only is distinguished by its comprehensive assembly and appraisal of knowledge on the subject, but by the facility of its author in communicating ideas. It has now been revised to incorporate changes that have taken place during the past decade.

Although Dr. Klein's views stem primarily from British experience and practice, the author's perceptiveness of developments in the U.S., as well as elsewhere in the world, contributes a universality to his treatment of the subject matter.

What was originally a 621-page single volume of 15 chapters is now offered as a three-volume edition. This review is concerned with the third volume, titled "*River Pollution-3: Control.*" Its 484 pages are an expanded version of four chapters from the original and one additional chapter dealing with pollution of tidal and coastal waters.

Incidentally, the other two volumes in the series, which were published earlier and are not dealt with here, are titled, *River Pollution-1: Chemical Analysis* and *River Pollution-2: Causes and Effects*.

Quite appropriately, the book opens with a discussion on the methodology of detection and measurement of pollution. Describing all aspects of physical,

chemical, bacteriological, and biological testing, not the least virtue of these discussions is the accompanying evaluation by the author (himself a chemist) of the merits and limitations of various diagnostic procedures. The instrumentation of river-quality monitoring is dealt with rather sparsely; but this comment reflects a personal prejudice—because of my preoccupation with this new technique—rather than a criticism of the author. Of special interest, in view of increasing attention to problems of estuarial pollution, is an assessment of considerations relating to the making of such surveys and measurements.

This is but the prelude, however, to an entire chapter devoted to studies on the degradation and cleansing of tidal and coastal waters, which Dr. Klein modestly asserts to be simply an introduction to the subject. In so saying, he focuses attention on the findings that have emanated from years of investigations conducted on the Thames Estuary by the British Water Pollution Research Laboratory (summarized in *Technical Paper No. 11*, published in 1964 by Her Majesty's Stationery Office).

Theory and technology of abatement of pollution by means of sewage and industrial-waste treatment comprise about a third of the book. Practitioners in the field must applaud this section as providing a remarkably useful compendium of available processes and their performance characteristics. Perusal of these pages would be revelatory to those who have only recently "discovered" the pollution problem and have been disclaiming that anything new has been developed in treatment technology over the past 50 years.

What also is made apparent is that there is more to the treatment of wastes than the abatement of pollution. Salvage of by-products from so-called waste waters has long claimed attention in Europe, as is documented by references to the practice of land disposal of sewage for enhancement of crop

production as early as 1543 from a community sewer in Bünzlau, Silesia, to the proposal advanced in 1961 for the use of sludge-digestion gas (methane) in the operation of a fuel cell for the production of electricity. Potentialities for recovering soluble fertilizing constituents in sewage effluents (notably nitrogen compounds and phosphate salts) through algae harvesting practices, or by the controlled growth and composting of water hyacinth plants, are among the many matters touched upon.

Standards

For those pondering the question of river standards and regulations for their implementation—and at present that embraces just about everybody in the United States including representatives of historical land-mark associations and anti-poverty leagues—a perusal of Chapter 5 will be illuminating. Here are detailed experiences over a half century in England in the endeavor to come to grips with this matter. Ample support will be found for the view that the promulgation of appropriate standards is a formidable exercise, to say nothing of the task of administering them.

The final chapter offers a nicely reasoned summary of the present situation and future prospects with respect to management of river quality. Pointing out that the discerning reader may well wonder why, since the passage of so much legislation in Britain, river pollution still goes on, Dr. Klein observes that laws are only preliminary stages toward control and offer little guarantee that pollution will cease. And he is not at all impressed with the application of penalties, saying that even in Russia some textile factories have preferred paying annual fines for polluting streams rather than finance the construction of waste treatment facilities; this is the argument advanced in this country to current proposals that the imposition of

"effluent charges" will provide incentive to industries to abate pollution.

Better look

Commenting on what he terms the "rather unbalanced and extravagant statements made in some quarters about the pollution of British rivers, Dr. Klein cites data compiled by the Ministry of Housing and Local Government regarding the conditions of nontidal streams in England and Wales. From this it is revealed that 73% of the total river mileage can be regarded as relatively unpolluted (less than 3.0 p.p.m. of B.O.D.), and 15% is of doubtful quality (3 to 12 p.p.m. of B.O.D.). The remaining 12% of mileage—mostly in the highly industrialized stretches of rivers—is classified as polluted or grossly polluted. What should be surprising, he says, is that this figure is not much higher!

His final conclusion is this: Much will be accomplished as a result of intensified efforts to alleviate the pollution of streams, but the most that can be expected with a large number of grossly polluted rivers flowing through highly industrialized areas is a marked reduction in the pollution. In brief, says Dr. Klein, "... pollution, like disease and many of the social evils and intractable problems of this age—crime, teenage delinquency, litter, drug addiction, road accidents—may eventually be brought under better control but is unlikely to be completely eliminated. And it must be emphasized that river purification is bound to involve heavy financial expenditure. Any major improvements in the condition of our rivers can only be brought about gradually; they will have to be paid for in the long run by the general public out of taxation ..."

for more than a decade. The League very early recognized that water is a national problem, requiring the best efforts of all levels of government at a time when the exercise of federal power in the field of pollution abatement was recognized by only a very few.

Historically, water pollution was considered a matter of local or state concern. The concept of federal responsibility in the water pollution field became evident in 1948 when the Water Pollution Control Act was passed, only to receive a serious setback in 1960 when then President Eisenhower vetoed an amendment to a federal pollution control bill because he believed that polluted water is a uniquely local blight and that the states should have responsibility for its control.

It was not until July 1961, that the national responsibility for water pollution control was formally recognized with President Kennedy's signing an amendment to the 1948 act, adding authority for federal action on intrastate streams and navigable waters. (For a summary of pollution control legislation in the U.S., see ES&T, January, page 18.)

Although the League as a whole chose water resources as a major study for subject and action a bit more than a decade ago, state and local Leagues had already been investigating and acting upon such problems as local sewers and water supply, state programs for pollution control, and coordination of state water agencies or state construction programs. It was from these widely varied operations of the local League groups, that the League came to recognize the national aspects of water as a resource.

This book makes the reader consciously aware of the national aspects of the water problem by detailing many case histories developed by the local League groups. The book, generally, is organized along major headings in which the problems are stated and dis-

No Lysistrata-like Threats, Just Facts

The Big Water Fight. General Editor, Suvia P. Whittemore, for The League of Women Voters. ix + 246 pages. The Stephen Greene Press, Brattleboro, Vt. 05301. 1966. \$6.95, hard cover.

Two complementary points of view dominate this very readable, well-documented, carefully prepared discussion of the League of Women Voters' separate and joint activities with all other interested groups in assuring adequate supplies of acceptable water throughout the U.S. On the one side, the League book notes: "Pollution is a natural process; no surface or ground water is pure H₂O. But man is a great polluter, and modern man is the greatest polluter of all. His multiple and varied pollutants are entering the U.S. rivers, lakes, and ground water, increasingly limiting the water's usefulness."

On the other side, the League says: "Decisions concerning water resources

are made within a complicated political process, through interaction among many groups: experts in and out of government, elected officials, political parties, private lobbies, and citizen groups. This process of interaction goes on in every level of government. It also travels up and down along the many lines of communication between local, state, and federal levels. The citizen who is willing to jump into this maze of criss-crossing influences will find plenty of opportunities to use his political pressure effectively. It must never be forgotten that water is a political problem."

No Jennies-come-lately to the conservation scene, the League of Women Voters have been surveying the many problems, recommending solutions, pushing for legislation, and informing the citizenry, the business community, and the politicians about water matters

cussed and then followed by a succession of fascinating and pertinent case histories.

The most detailed of these case histories is the one which appears as Chapter 6, "On the Edge of a Big City," a reproduction of a basin study by 14 Leagues of the Sudbury-Assabet-Concord River Basin adjacent to Boston. This chapter and the one following it reveal the great depth and attention to detail that characterizes many of the League's activities—both in the matter of water resources and in many of the others it chooses to pursue.

There is no doubt that the League members have done their homework well. Their approach is well-informed, dedicated, realistic, and effective. They have managed to get the active participation of all interested groups in working together to evolve an adequate and operable program. The information presented in Chapters 6 and 7—as well as in the other case histories—reveals the careful planning, diligence, and remarkable foresight of the League.

Potato-sugarbeet controversy

Typical of the many case histories that dot the book with telling effect is the potato-sugarbeet controversy in Maine just a few years ago. At that time Maine was in the throes of classifying its lakes, rivers, and streams on the basis of receiving-water standards. Under this concept, discharge of wastes—even raw sewage—into a stream is permitted, provided the quality of the stream is maintained within certain limits.

Although the classification had been reasonably accomplished, there were many niggling problems to be solved. One involved lowering a stream classification to accommodate a proposed sugarbeet refinery.

For years, Maine has been dependent on the potato crop. Therefore, the state fathers were delighted when they obtained from the U.S. Department of Agriculture a hard-to-get sugarbeet allotment, with a proviso that a refinery be built by 1966.

After long debate in the state council chambers, state officials proposed to put the sugarbeet processing plant next to an already established potato processing plant. The potato plant owner encouraged the presence of the new neighbor and offered the use of his treatment plant until adequate facilities

could be installed. But there was the conundrum: The potato plant processor was not adequately treating his effluent; and the material from the new plant would make the discharge into the stream even more contaminated. But what to do? The plant had to be built in a certain time or else the sugarbeet allotment would be removed. The water classification system was about to be tampered with. The plant operator had only made token improvements in his treatment facilities, which were grossly inadequate even for the plant's own wastes, and could never handle anything new.

The League book sums up the situation in this way: "So the potato plant and the sugarbeet plant are tied together in a confused picture at the moment. Will the Attorney General issue an injunction? Will in-plant processes be tried as long as the [current] classification is being met? Will the citizens downstream ban together in effective protest? Is anyone willing to oppose the potato plant owner, who, after all, is providing 10½ months' employment each year for several hundred people who formerly had only a few months each year of seasonal employment? Will both the potato plant and the sugarbeet plant eventually put their houses in order so that the [stream] can again become [the higher classification stream]? These are the knotty questions, involving economics, political decisions, and value judgments. All across the nation similar questions will have to be met, face on."

Paying the price

And this, says the League, is the nut of the problem. How fast the country moves toward upgrading its lakes, streams, and coastal waters, and in what way it chooses to pay the costs, will continue to be a lively and complex challenge to the nation. Treating water as a reusable resource involves river basin planning, notes the League. And it means investigating area needs and determining how best to satisfy these needs to speed the development of water resources and related land resources. Basic planning involves irrigation, flood control, navigation, hydroelectric power, municipal and industrial water supply, pollution control, recreation, and conservation of natural areas, fish, and wildlife.

In its enlightened approach to the

water-resources program, the League observes that the choices are seldom black or white. Indeed, there may be a choice among two or more solutions, equally feasible from an engineering point of view and offering quite different lines of future development. Making these choices is a political problem which the voter should understand and weigh carefully, because the direction in which he exerts his support and the way he casts his vote will have far-reaching economic, political, and social ramifications. By turning his back he cannot stop the decision-making process.

Citizen participation

The question is whether these important decisions will be made with or without the benefit of his—the citizen's—point of view. When the League says: "When Americans were fewer, the cities and industrial plants were smaller and farther apart, our stream and river systems could carry off the waste materials and still provide satisfactory water for people downstream. The great capacity of flowing water to clean itself may be simple; but it made it simple, natural, and reasonable for people to use streams and rivers to dispose of domestic and industrial waste. The situation is no longer tolerable, or even feasible, for water pollution is not so much a water problem as it is a people problem," the League carefully documents its case. No Lysistrata-like threats, just facts.

New Staff Member Appointed



Nancy M. Campbell has joined the staff of ES&T as an editorial assistant. Mrs. Campbell will devote her efforts to the writing and editing of material for the staff-generated portions of ES&T, and will assist in layout and production through liaison with the art and production departments. Mrs. Campbell comes to ES&T from John I. Thompson & Co. (Washington, D.C.) where she worked since 1964 as writer-editor in such fields as electrochemistry, biology, physics, mathematics, and medicine. A student at Mount Saint Agnes College (Baltimore) in their science and mathematics curriculum from 1959-63, she transferred to the University of Maryland to complete her degree in English and history, studying there from 1964-66. Among her work experiences Mrs. Campbell also includes a tour of duty as a medical laboratory technician at Easton (Maryland) Memorial Hospital.

MEETING GUIDE

April 6-8
**Columbia University, HEW,
Polytechnic Institute of Brooklyn**

Power Systems for Electric Vehicles

Ferris Booth Hall, Columbia University,
New York, N.Y.

Aimed at covering the broad aspects of technical and social problems related to development and use of electric vehicles, papers will be directed specifically to such things as system energy needs, impact on urban areas, and new concepts and technologies for fuel cells and batteries.

April 9-14
American Chemical Society

153rd National Meeting
Miami Beach, Fla.

In addition to the many papers at the 153rd National Meeting that will touch on matters of interest to those involved in environmental studies, there are two special symposiums dealing exclusively with such matters.

Symposium on Trace Inorganics in Water. Invited papers only. Divided into three major sessions, the symposium will include fundamentals, applied, and analytical considerations involved in the study and understanding of trace inorganics in water.

Symposium on Water Chemistry (Joint with Division of Chemical Education) Invited papers only. The theme of this symposium is the role of chemists in the study of natural waters, water and wastewater treatment, and water pollution control. Areas of water chemistry included in the symposium are analytical methods, municipal and industrial water treatment, water pollution control, ground water, lakes, rivers, and marine waters.

Three additional Division of Water, Air, and Waste Chemistry programs also bear on problems of environmental research and development:

Scientific Information Resources for the Water Researcher (Joint with Division of Chemical Literature)
General Papers, Water
General Papers, Air

April 10-12
Institute of Environmental Sciences

1967 Technical Meeting and Equipment Exposition

Shoreham Hotel, Washington, D.C.

The meeting is divided into a technical section and a tutorial section. The technical section will include sessions on environmental management and equipment, simulation instrumentation, space, earth, and marine environment, and the specialty areas of dynamics, electromagnetic interference, and thermo-environment associated with high speed flight. The tutorial section will be directed to marine and space environments and instrumentation techniques.

April 17-19
**Technical Association of the
Pulp and Paper Industry**

TAPPI 4th Water Conference

Benjamin Franklin Hotel, Philadelphia,
Pa.

Covering such subjects as water reuse, water supply and treatment, and sludge disposal, the TAPPI meeting will also be the occasion for discussions of a recently completed survey of costs for effluent disposal in the pulp and paper industry, as well as a new (second) report on the TAPPI water division reuse questionnaire.

April 24-26
American Medical Association

National Congress on Environmental Health Management

Americana Hotel, New York, N.Y.

The congress will explore concepts, functions, and responsibilities involved in the development of integrated research programs and the full utilization and coordination of professional, administrative, and technological resources on environmental problems and requirements.

May 1-5
**American Industrial Hygiene
Association, American Conference of
Governmental Hygienists**

American Industrial Hygiene
Conference-1967

Pick-Congress Hotel, Chicago, Ill.

In addition to a wide-ranging program on matters pertaining specifically to health, the conference plans sessions on air pollution, atmospheric diffusion, sulfur dioxide, abatement, noise effects and controls, radiation hazards and controls, stack design, and building re-entry of fumes.

May 2-5
New York Academy of Sciences

Biological Effects of Pesticides

Waldorf-Astoria Hotel, New York, N.Y.

The conference is directed especially to members of the scientific community who are in a position to contribute to the further sophistication of research on health and related aspects of pesticides. Conference participants will include world authorities on toxicology, metabolism, mode of action, and epidemiological effects of pesticides.

May 15-17
**U.S. Atomic Energy Commission,
Ecological Society of America,
University of Michigan**

Second National Symposium
on Radioecology

Horace H. Rackham Lecture Hall,
University of Michigan, Ann Arbor,
Mich.

Subtitled Nuclear Energy in Man's Environment: Past, Present, and Future Problems, the symposium is designed to acquaint ecologists with the problems arising from the release of radiation to the environment—and how such problems have been treated in the past, so that future radiation hazards may be dealt with adequately.

May 15-18
**American Association for
Contamination Control**

Sixth Annual Technical Meeting
and Exhibit

Sheraton-Park Hotel, Washington, D.C.

Contamination control problems and solutions that are typical of hospital operating rooms, pharmaceutical and biological laboratories, and industrial and aerospace clean rooms will be discussed.

June 1-2
**Vanderbilt University School of
Engineering**

Sanitary and Water Resources
Engineering Conference

Noel Hotel, Nashville, Tenn.

In addition to sessions on water resources engineering, design and operation of treatment processes for municipal and industrial wastes, and hydraulic and hydrologic aspects of waste water collection and disposal systems, a special session will be devoted to atmospheric pollution and control.

June 4-9
American Water Works Association

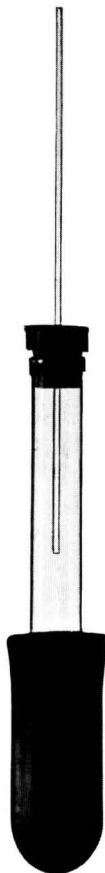
87th Annual Conference

Atlantic City, N.J.

Sessions on water resources will focus on federal and state action to develop programs to ensure an adequate water supply for the nation. Included will be a program on the Grand Canal Project to divert seven Canadian rivers into the Great Lakes and the Long Island Dam Project to dam both ends of Long Island Sound to make it into a fresh-water reservoir.

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MEETING GUIDE continued

June 11-16
Air Pollution Control Association
60th Annual Meeting

Sheraton-Cleveland Hotel, Cleveland, Ohio

Technical sessions will be directed at such things as air pollution and the professional chemist, long-lived pollutants, experimental exposures, personnel and training, air quality control, equipment, solid wastes, meteorology, and odor.

June 11-16
National Research Council
(Division of Biology and Agriculture)

International Symposium on Eutrophication

University of Wisconsin, Madison, Wis.

The symposium will review the status of world knowledge of the problems of eutrophication, the aging of lakes and streams brought about by natural or man-induced forces. Invited papers will be presented by 36 international specialists in the fields of botany, chemistry, limnology, zoology, hydrology, and sanitary and agricultural engineering. The meeting will serve as a forum for an exchange of views on the problems and will include discussions of public policy and the broad social and economic consequences of eutrophication. At the conclusion of the meeting an executive session will be convened to prepare recommendations for action.

June 12-16; 26-30
Manhattan College, Federal Water
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Manhattan College, New York (Bronx), N. Y.

The institute is divided into three courses: Stream and estuarine analysis, June 12-16; Physical and chemical waste treatment, June 12-16; and Biological waste treatment, June 26-30. Fee for each course is \$150, but stipends and travel allowances are available for qualifying U.S. citizens. Write: Donald J. O'Connor, Civil Engineering Department, Manhattan College, New York, N.Y. 10471.

June 15-16
U.S. Departments of Agriculture and
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Jefferson Auditorium, Department of Agriculture, Washington, D.C.

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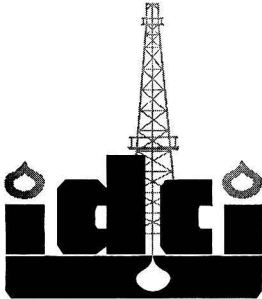
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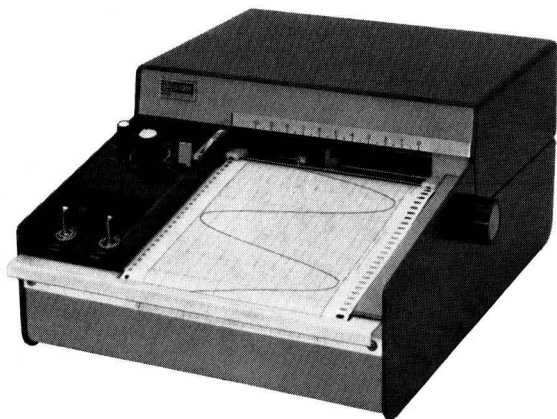
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