Environmental Science & Technology

APRIL 1973

Burn garbage burn
308

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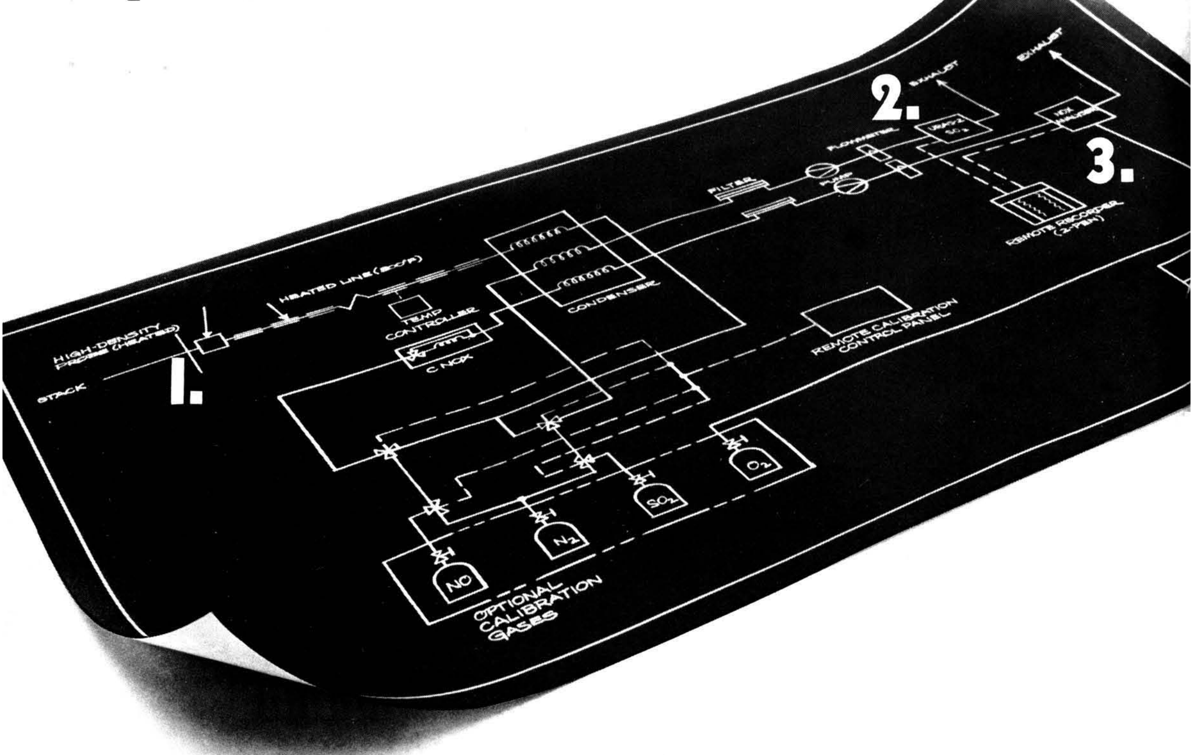

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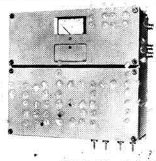

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Volume 7, Number 4, April 1973

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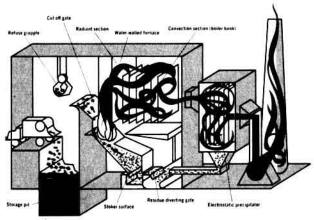

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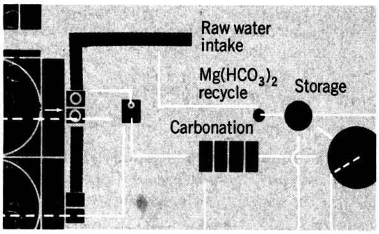

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RESEARCH BRIEFS

C. Paul Falls and Louis Varga of the Oklahoma State University discuss chemical equilibrium models for Oklahoma's Lake Keystone 319

Models have been developed to depict the concentrations of all principal inorganic chemical species in this lake. Agreement is good between the values predicted by the model and actual chemical and physical observations made in 1966-68.

A kinetic study of phosphate reaction with aluminum oxide and kaolinite is detailed by Harvard University's Y. S. R. Chen, James Butler, and Werner Stumm 327

Aqueous phosphates in lake waters can be adsorbed by alumina and kaolinite. The high phosphorus binding capacity of sediments is correlated with high clay mineral content of the sediment. An initial rapid adsorption step is followed by a slow process.

A new technique for the removal of chromate from cooling tower blowdown is reported by E. I. Onstott and William Gregory of the Los Alamos Scientific Laboratory and Edward Thode of the New Mexico State University 333

Many users of the proved chromate corrosion-prevention method have chosen to abandon it rather than go to the expense of special waste treatment facilities. The new method of treating cooling tower blowdown uses electrochemically generated ferrous hydroxide as the reducing agent. The method works without adjusting the pH of the blowdown before or after electrolysis.

Russell Dietz and Edgar Cote of the Brookhaven National Laboratory (Upton, N.Y.) trace atmospheric pollutants by gc determination of sulfur hexafluoride 338

The complex nature of dispersions from single point sources, tall stacks, cities, and highways can be followed using the SF_6 tracer technique. This technique can also be used to determine and evaluate short-time exposure to high-level doses or concentrations, and whether a nuclear power plant stack effluent meets AEC ground level radioactive exposure doses.

Decomposition rates of ozone in living areas are summarized by Frank Mueller, Leopold Loeb, and William Mapes of the GE Co. Major Appliance Laboratories (Louisville, Ky.) 342

The decomposition of the air pollutant ozone in living areas depends on a number of variables—temperature, relative humidity, and the number of active catalytic surfaces in a room. Activated carbon filters are effective in keeping the ozone concentration to acceptable levels in living areas.

Cal Tech's Rolf Sabersky, Daniel Sinema, and Fredrick Shair on concentrations, decay rates, and removal of ozone and their relation to establishing clean indoor air 347

Rubber, fabrics, and plastics decompose ozone much more rapidly than metals and glass. Activated carbon filters can be used to reduce indoor levels of ozone well below the maximum acceptable limits. Considering that a person spends 80% of his time indoors, reducing the pollution level in buildings results in less personal exposure.

NOTES

Marquette University College of Engineering's Seitz, Riedner, Malhotra, and Kipp identify an iron-phosphate compound in sewage sludge residue 354

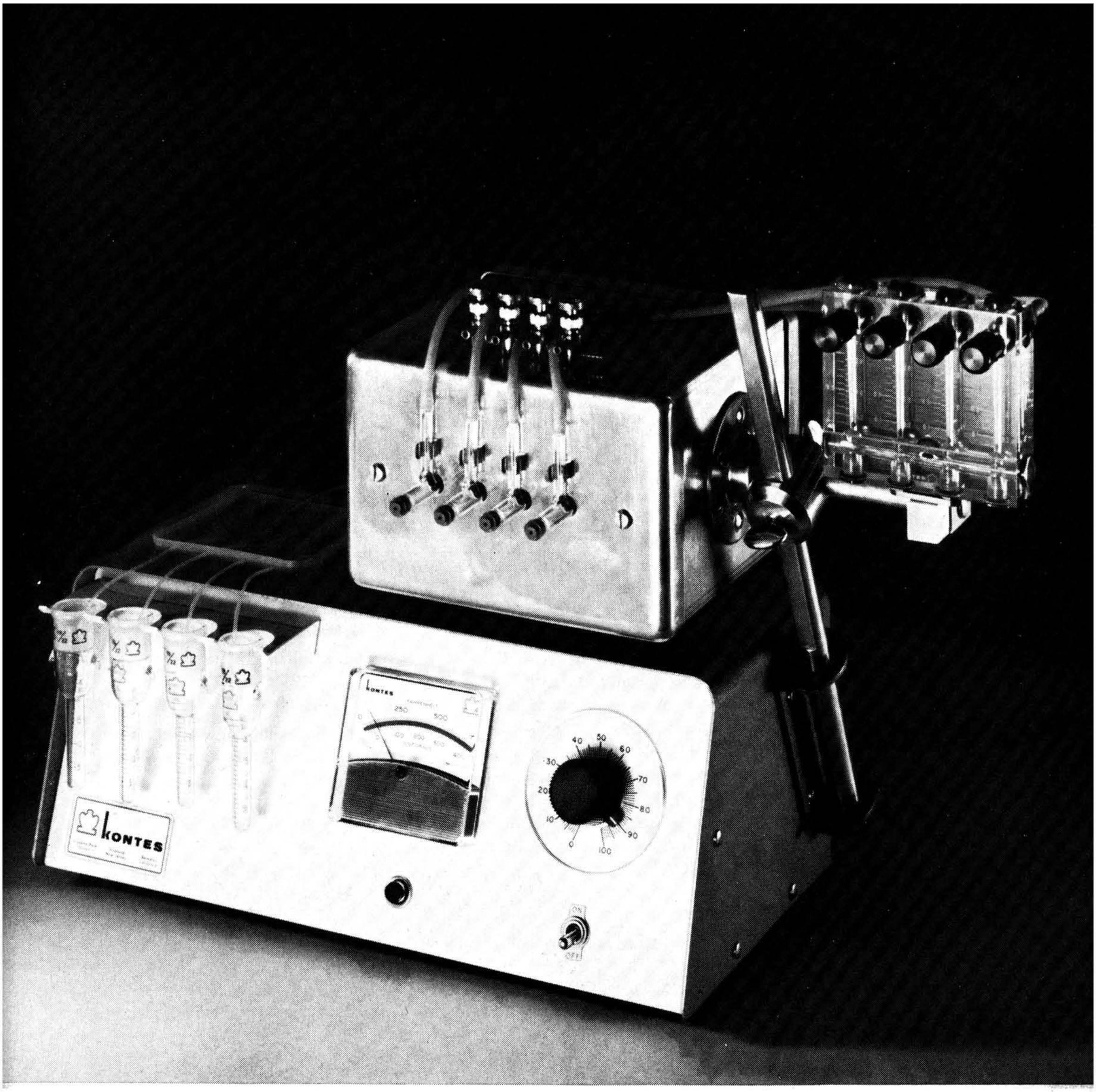
The iron phosphate compound, vivianite, has been found at about the 1% level in the dried sludge from the Milwaukee Jones Island sewage treatment plant. Phosphate removal at this plant occurs by the formation of vivianite. Being magnetic, vivianite was recovered by a magnetic separation scheme and identified by X-ray diffraction.

The fallout of heavy metals around a power plant is characterized by David Klein and Philip Russell of the Hope College Department of Chemistry 357

The soil around a coal-fired power plant on the eastern shore of Lake Michigan was found to be enriched with 10 metals, including cadmium, mercury, and zinc. With the exception of mercury, the soil enrichment was related to the metal content of the coal burned in the power plant.

Credits: 287 (top right), North American Rockwell; 289, U.S. Forest Service; 291, Air Products and Chemicals; 293, 294, *ES&T*'s Marty Malin; 296 (lower), *ES&T*'s Carol Lewicke; 299 (top), UPI; 299 (bottom), *C&EN*'s Fred Zerkel; 300, Phorbes Photos; 310 Detroit Stoker Co.

Cover: John Sinnett



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Reference J. O. A. C., Vol. 48, Dec. 1965, "A Sweep Co-Distillation Clean-up Method for Organophosphate Pesticides", by **R. W. Storherr & R. R. Watts. ® Trademark of Du Pont

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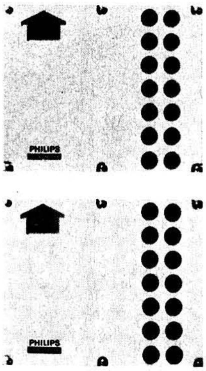
PHILIPS
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EDITORIAL

To treat or reuse, that is the choice

Between now and hopefully by 1985, the discharge of pollutants into the navigable waters will be eliminated, according to the national game plan P.L. 92-500. During the interim, industries and municipalities will have to improve the treatment and ultimately perfect the complete reuse and recycle of their waters.

At what point does it become more economical to reuse than to treat and dispose? To what extent are municipalities and industries practicing reuse today? What industries, what municipalities are exemplary, setting the pace, and showing the way?

This month's feature author Witmer calls attention to the fact that desalting technology, with suitable modification, can be used for water reuse applications. Sure, some of the equipment has been used in rather specialized and at the same ttme rather small-scale applications. In fact, most of the uses have been predicted on the goal of meeting water quality standards. Nevertheless, the age of large-scale deployment of such equipment is dawning. Witmer discussed promising technologies that both industries and municipalities may find useful for such purposes.

Later this month, a symposium in Washington, D.C., on water reuse will be co-sponsored by the American Institute of Chemical Engineers and the Environmental Protection Agency. Only last month, WWEMA (the trade association for some 300 equipment manufacturers and suppliers) held its first conference on industrial waste water treatment in Chicago.

Again, the reuse terms must be clarified. For example, reuse for the same process, reuse for another industry, or reuse for drinking water purposes. Eventually, attention must be paid to the problem of ultimate disposal—i.e., the residual left after the last drop of water has been recovered from the waste effluent.

The name of the game is to treat, but the new emphasis on reuse will continue to become even more popular in the future.

Stanton Miller

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For author's guide and editorial policy, see June 1972 issue, page 523 or write Norma Yess, Manuscript Reviewing Office.

In each paper with more than one author, the name of the author to whom inquiries should be addressed carries a numbered footnote reference.

LETTERS

Fragile environment

Dear Sir: The article, "Waste Control in a Fragile Environment," in the November 1972 issue deals with the environmental problems created by elemental phosphorus discharged with effluents from E.R.C.O. at Placentia Bay, Newfoundland. Although the company has a pollution abatement program under way, all the problems have not been solved and the direct discharges of elemental phosphorus have been greatly reduced but not eliminated. There are also air pollution problems associated with the plant which we will endeavor to solve in concert with the Provincial Authorities. In addition, while Placentia Bay is open to fishing, a productive portion of Long Harbour (where the phosphorus plant is located) remains closed to commercial fishing because of the potential threat of contamination.

Jack Davis
Minister
Environment Canada
Ottawa, Ont.
Canada KIA OH3

Hazardous chemical spills

Dear Sir: Arthur D. Little, Inc. is in the process of developing a hazardous chemical spill response manual for the U.S. Coast Guard. A complete listing of available oil and chemical spill countermeasure equipment with particular emphasis on chemical spill control techniques is needed. Containment booms, skimmers, chemical dispersants, sinking and jelling agents, acid neutralizing materials, and any other response systems will form an integral part of the handbook.

Any manufacturer or supplier who wishes to be listed in the handbook is requested to send us descriptive brochures, technical data, any available details on past utilization at an oil or chemical spill site, and, if possible, a listing of customers by geographical location.

J. Leslie Goodier
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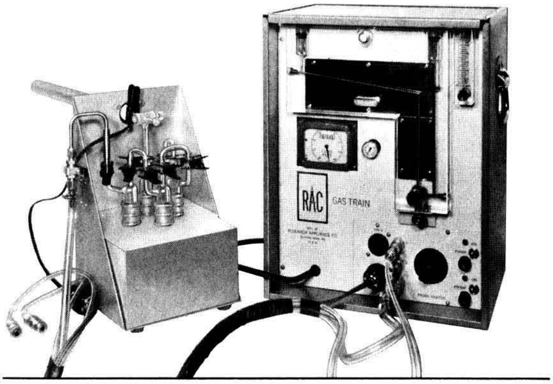
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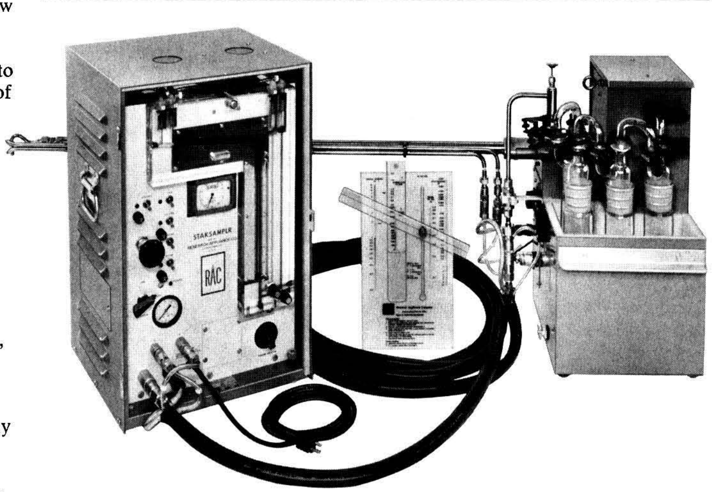
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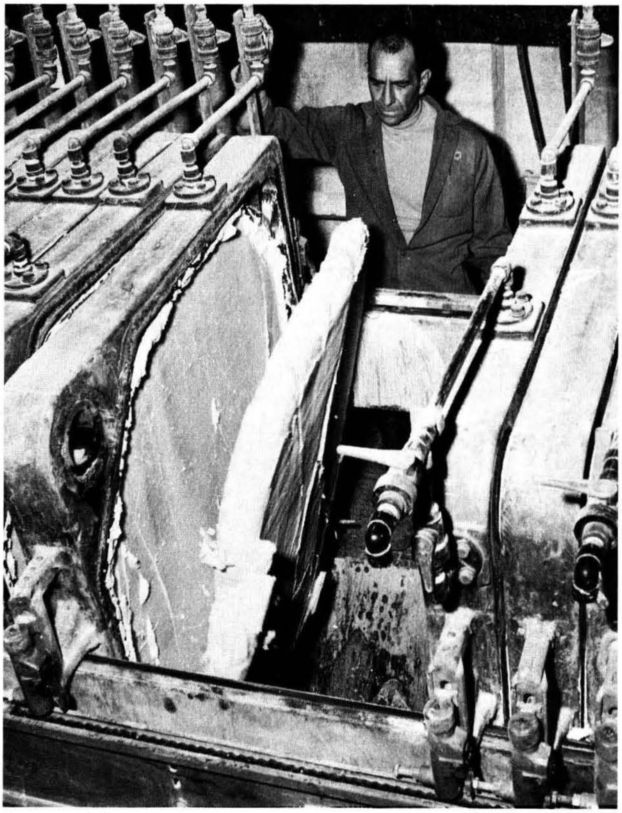

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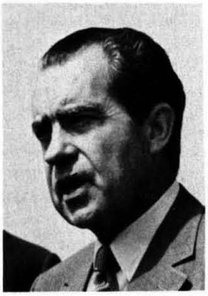
CURRENTS

WASHINGTON

President Nixon's 1973 State of the Union Message was divided into a number of sections, the first of which dealt with the environment and natural resources. He said, "Now there is encouraging evidence the U.S. has moved away from the environmental crisis that could have been and toward a new era of restoration and renewal." He continued, "Year by year, our commitment of public funds for environmental programs continues to grow; it has increased fourfold in the last four years. In the area of water quality alone, it has grown fifteen-fold." The message included 19 proposals for additional environmental legislation proposals including toxic substances, hazardous wastes, safe drinking water, sulfur oxides emission charge, sediment control, UN environmental fund, ocean dumping convention, and controlling the environmental impacts of transportation.



President Nixon

EPA's new national permit system, authorized under Section 402 of last year's water pollution control law (ES&T, December 1972, p 1068), requires industrial, municipal, and other point sources dischargers to obtain permits for the discharge of any pollutant into all navigable waters of the U.S. Dubbed the National Pollutant Discharge Elimination System (NPDES), the program involves some 40,000 of the nation's 300,000 industrial water users, some 10,000–13,000 municipal waste treatment sources, and additionally, other point sources such as feedlots and acid mine drainage. Effluent guidelines for industrial categories are being developed; they are due on the first anniversary of the new law.

EPA finds that three noncatalytic auto emission control systems will meet the 1975 standards. In its staff study which summarizes the auto manufacturers' progress in meeting the standards, Honda's CVCC and Toyo Kogyo's rotary have demonstrated 50,000 miles durability at or below the 1975 emission requirements. The emission performance of these two systems has been verified by test at the EPA laboratory in Ann Arbor. Robert Sansom, EPA assistant administrator or for air and water programs says that the rotary engine with its estimated 35% loss in fuel economy could have a substantial impact on total gasoline consumption when it begins to be mass produced in the U.S.

The National Academy of Science also says automobile manufacturers will probably be able to meet the 1975 standards. In a report by its Committee on Motor Vehicle Emissions, four engines—the modified conventional engine equipped with an oxidation catalyst, the carbureted stratified-charge engine, the Wankel engine equipped with an exhaust thermal reactor, and the diesel engine—will probably meet the 1975 standards for certification and, in aggregate, can be mass produced in sufficient quantity to meet the 1975 market demand. In another report, from the National Academy of Engineering Marine Board, accidental releases of oil can be virtually—but never completely—eliminated by the consistent application of technical systems and methods of operation currently available to the offshore petroleum groups at the water depths in which they now operate.

Sediments at the rate of 1.3 million tons every day are added to the rivers in the 48 states, according to the U.S. Geological Survey. The Mississippi River alone discharges about a quarter of a million tons of sediment every year into the Gulf of Mexico—almost as much as all other U.S. rivers combined. USGS hydrologist William Curtis notes that sediment yields can be used to assess land use practices and are a good indication of the amount of sediment that must be dredged from harbors and channels to maintain navigation depths.

The National Industrial Pollution Control Council (NIPCC), one cooperative between industry and the Federal Government, will be three years old on the 14th of this month; its new chairman is Willard Rockwell, Jr. NIPCC takes a certain amount of credit for the strong commitment that U.S. industry has made toward pollution control. In the past three years alone, industry has spent $10 billion on its air and water pollution problems plus an additional $4 billion on research. Between now and 1976, the electric utilities industry, the petroleum industry, the chemical industry, and the steel industry will each spend at least $1 billion for pollution control—on top of all their previous large expenditures.

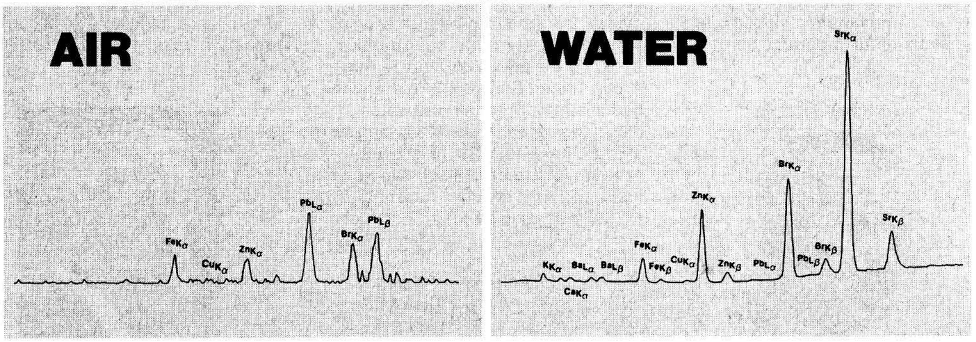
NIPCC's Willard Rockwell

STATES

Deepwater oil ports are unacceptable, New Jersey Governor William Cahill emphasized in a strongly worded statement rejecting Army Corps of Engineers proposals to build a port at any one of four locations in or di-

New Jersey's Governor Cahill

Another Major Advance in the Analytical Power of Energy Dispersive X-Ray Analysis



Particulates From New York City Air.
CONCENTRATION = $\mu g/cm^2$

Fe	Cu	Zn	Pb	Br
4.37	.54	1.60	6.10	2.12

Dried Plankton
CONCENTRATION = $\mu g/cm^2$

K	Ca	Ba	Fe	Cu	Zn	Pb	Br	Sr
69.04	47.60	42.30	18.91	1.10	26.20	0.73	35.00	67.55

A Finnigan QM-900 Automated Energy Dispersive X-ray Fluorescence Analysis System detected and quantified trace concentrations of iron, copper, zinc, lead, and bromine in an air pollution particulate sample in less than two minutes. The sample, on filter paper, was simply inserted into the instrument's sample chamber. Under X-ray excitation, atoms in the particulate matter fluoresced X-rays of different energy levels, depending on the element fluorescing. In 30 seconds, the QM-900 automatically summed up X-ray emissions of each element, subtracted background contributed by the filter paper, and displayed the elemental spectrum at the left. Under internal program command, each peak was integrated, compared to stored standards, and the identification and concentration of each element on the filter paper were printed out in $\mu g/cm^2$. Finnigan X-ray systems detect and analyze elements at concentrations less than 0.5 $\mu g/cm^2$.

The spectrum at the right shows a similar two-minute analysis of dried plankton from the Pacific Ocean off Monterey, California. In similar fashion, we have analyzed such other water pollution samples as sludge from the Houston Ship Channel and New York's East River, and effluent from a Georgia paper mill.

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rectly affecting New Jersey. An environmental impact statement projected massive development of petrochemical and refinery facilities, the need for large land areas for housing, increased pollution from new industries and additional population, shortage of water supply, and periodic oil spills.

New Jersey Senators Clifford Case and Harrison Williams have introduced a bill into Congress that would require that a complete report with respect to any proposed offshore facility be submitted to EPA for approval. Also, the Governor of each adjacent coastal state which might be affected in any way by the project would have 90 days in which he could veto the project before the facility is approved, licensed, or constructed by any federal department or agency.

A waste disposal system at Port of Indiana/Burns Waterway is now operating and serving as a prototype for pollution control facilities for other U.S. ports. A treatment plant handles sewage, bilge, and ballast water which is piped to the plant for oil skimming, aeration, coagulation, settling, and phosphate removal.

Oregon's "bottle bill" which requires a deposit on all beer and soft drink containers "has failed to achieve its purpose of decreasing container litter," claims R. Thomas Willson, senior vice-president, American Iron and Steel Institute. Since the law went into effect last October, beverage containers increased from 14.4% in September to 18.2% of litter by piece-count, according to surveys. The growth in volume of beverage containers increased from 17.3% to 24.5%. The bill, Willson adds, damages "the beverage and packaging industries serving the people of Oregon."

Industrial wastes and hazardous substances discharged into Wisconsin's air, water, and soil are now monitored in a program which became effective in February. The state's Department of Natural Resources requires all persons except municipalities to make regular reports of the kinds and amounts of industrial wastes or toxic or hazardous substances they discharge. The monitoring program's goal is the development of an effluent directory that will list where, when, and in what quantities pollutants are released.

Ten major oil companies had requested a variance from New York City's strict limits on the lead content of gasoline, but the request was denied by Environmental Protection Administrator Jerome Kretchmer. New York's Air Pollution Control Code, passed in 1971, mandates a stepwise reduction in the lead content of gasoline. Last year, only 1 gram lead/gal of gasoline was allowed, and this year, 0.5 gram lead/gal was the limit from which the oil companies sought relief. By January 1974 no lead will be allowed. Under the terms of Kretchmer's decision, the oil companies had to supply regular gasoline by this month and premium gasoline by June 28 in compliance with regulations.

Maryland's Department of Natural Resources has adopted two regulations for wild lands management and protection. One regulation specifies that wild lands (undeveloped lands not protected by wilderness statutes) shall be protected from fire, insects, and diseases at the same standards as other state lands with minimum disruption of the lands. The other ordinance limits and eventually phases out the use of motor boats in wild lands. The regulations become effective in July.


Wild lands

Drinking water is under scrutiny in New Jersey. Its Department of Environmental Protection has initiated legal action against six suppliers of drinking waters who failed to comply with potable water regulations. The department is seeking compliance with the regulations in the interest of safety of public water supplies.

TECHNOLOGY

A combination incineration-pyrolysis process to turn solid waste into gas will get a major demonstration at Orchard Park, near Buffalo. The EPA-sponsored tests will use technology developed by Torrax Systems, Inc. In this process, wastes are dumped into a large shaft-furnace where they are gasified by blasts of 2000°F air. The organic fraction of the wastes begins to decompose and most of the waste volatilizes into gas. Nonvolatile organics are then burned, and nonburnable residues settle as a molten slag. The slag is water-quenched and forms a granular material which can be used for building blocks and insulating fiber or aggregate for highway construction. Off gases are burned to raise steam for power generation. Present costs of the pyrolytic combustion process are $12-14/ton but those could drop to $5-6/ton in commercial operation. Sale of steam and slag could reduce costs further.

Smoke and gas emissions from coke ovens during pushing and quenching can be eliminated with a system developed by Halcon. The hooded quench car system, nicknamed "Puff the Magic Dragon," uses two specially equipped railroad cars coupled together. Hoods capture emissions from the pushing operation and move them through ductwork connected to a trailer car. Gases and smoke are drawn into a cleaning system, and dust and other contaminants scrubbed from the hot gases are separated in a demisting unit. The water removed by the unit is recycled and used for quenching, and clean gas is vented to the atmosphere. Dust is collected in a special hopper on the trailer car. Formally called the Hanley/Allen hooded quench car system, "Puff" is undergoing tests at a coking operation in Chicago owned by Interlake, Inc.

Plastics which can be tailor-made to photodegrade over time periods ranging from a few days to six months or more are now being marketed by Van Leer Ecoplastics, Ltd. (Canada). Dubbed Ecolyte, the company claims the plastics are unique since the system is not based on an additive but on a new polymerization process. Key to the Ecolyte process is the incorporation of ketone groups in the monomers used to make the plastics. These groups absorb radiation from the sun but do not absorb

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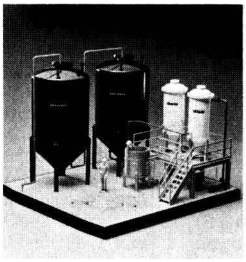

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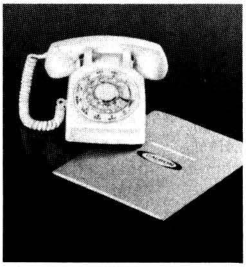

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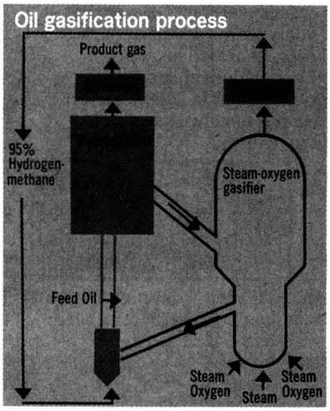
visible radiation. When exposed to natural sunlight, Ecolyte plastics become brittle, break up, and become part of the soil, susceptible to further biological decomposition. The plastics eventually end up as carbon dioxide and water.

A new oil-gasification process for producing substitute natural gas (SNG) from low-cost feedstocks is more economical than present methods, according to The Institute of Gas Technology. Other oil-gasification processes rely on naphtha and LPG as feedstocks. In the new process, feedstocks such as low-grade crude or residual fuel oil are reacted in a fluidized bed medium in a hydrogen-rich atmosphere at elevated temperature and pressure. The fluidized bed solids serve as a heat carrier and also trap excess carbon from the low-grade oils. The carbon-coated solids are circulated to a second vessel where they react with steam and oxygen to produce hydrogen. The new process also includes stages for removing carbon oxides from the hydrogen steam and for purifying SNG. The 20-year average selling price of the gas at the gate would be 85¢/million Btu, using Bunker "C" at $2/bbl.



Laser light can wipe out water hyacinths or other plants selectively in water or on land, says Ralph Scott, chief chemical scientist for DOD's explosives safety board. The laser light eliminates the need for long-lasting chemicals. Scott, who patented the laser-based, plant-destroying device, has licensed his invention to federal, state, and local governments on a royalty-free basis.

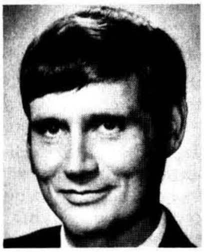
INDUSTRY

The feasibility of a second natural gas Canadian pipeline to transport potential reserves of natural gas from some Canadian Arctic islands is being studied by a group of Canadian companies. The consortium, consisting of Trans-Canada Pipelines Ltd., Panarctic Oils Ltd., Canadian Pacific Investments Ltd., and Tenneco Oil & Minerals Ltd. will continue a study begun last year by Panarctic Oils to determine the best route for bringing natural gas to Canadian markets. Panarctic has discovered about ⅓ the amount of gas reserves necessary to keep a pipeline in operation on Melville Island, King Christian Island, and Ellef Ringnes Island. Such a pipeline would need 25–30 trillion ft^3 of proved reserves to be economically viable.

The U.S. textile industry is waiting for the "uncertainty" surrounding pollution control standards to be resolved before investing heavily in pollution control programs. According to The National Industrial Pollution Control Council the "result of this uncertainty has been that many companies delayed building waste treatment systems that could have been in operation earlier." Because of the textile industry's great diversification of manufacturing processes, pollution control has been more of an individual company effort than it has been an industry-wide cooperative program. Overall, the textile industry contributes about 1% of the total waste water discharged annually by U.S. industry; large numbers of plants are in New England, along the Mid-Atlantic coast, and the Southeast.

Bell Labs says its base metal catalysts, touted several months ago as an effective device for converting carbon monoxide into carbon dioxide, is particularly effective in converting nitrogen oxides into nitrogen. Its lanthanum lead manganite catalysts produce much less ammonia when tested at low temperatures than do conventional catalysts. The nitrogen oxide tests represent only a preliminary laboratory evaluation, and Bell stresses that "ultimate usefulness can be determined only by tests on real exhaust systems." A similar announcement by Bell earlier that its proprietary compound might "rival platinium" as a catalyst for removing carbon monoxide from auto exhausts, drew sharp fire from Englehard Industries on the grounds that tests had been carried out using only synthetic gas mixtures instead of actual auto exhaust (ES&T September 1972, page 776).

The key to paper recycling is to build large wastepaper and paperboard mills as near as possible to urban areas, according to a study released by Joseph E. Atchison Consultants (New York City). If recycling of paper is ever to become competitive, wastepaper must be segregated prior to refuse collection and reprocessed in mills close to populous metropolitan centers, the study finds. Present recovery rate for wastepaper is only 21% in the U.S., far below the 38% figure for Japan. Large-scale urban mill construction, improved wastepaper collection systems, increased consumer acceptance of products made from recycled wastepaper, tax and other legislative incentives, and shipping of reclaimed fiber to fiber-deficient countries could boost the recovery rate to 25–27% by 1985, 30% by 1980, and ultimately to the World War II high of 35% some time in the 1990's, the study predicts.



Air Products' McAuley

Oxygen plants could become "as common at waste water treatment plants as they are now at steel mills and chemical plants" during the next decade says William McAuley of Air Products and Chemicals, Inc. Oxygen-activated sludge processes such as Air Products's OASES and Union Carbide's Unox will depend heavily upon on-site oxygen generation. McAuley says that 15–100 tpd cryogenic oxygen generators will be needed for the majority of new waste water facilities being planned. (A 100-tpd generator makes enough oxygen for a 150-mgpd municipal plant.) For requirements in the 15–25 tpd range, particularly where oxygen use is highly intermittent, noncryogenic adsorption processes will be more useful, according to McAuley.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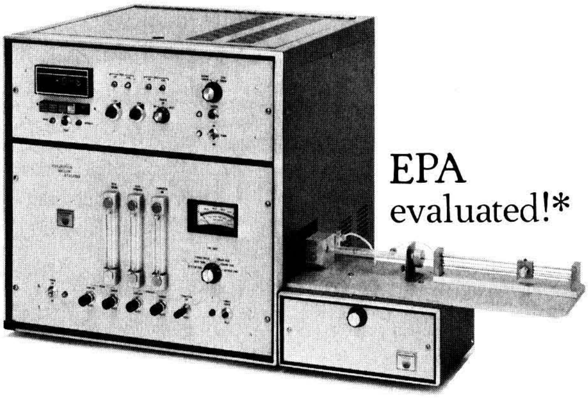


INTERVIEW

Waste Management's Harold Gershowitz

Waste Management bills itself as a "total systems" company—what does that mean? There are several aspects to waste management, of which only one would be the truck you see running down the street. In addition to that truck, one has the opportunity to provide a storage system, a containerization system for the waste before it gets to the truck, and possibly a stationary compaction system to feed waste into the truck. Once it's in the truck, in a total system, you may also provide the processing—compaction and transfer system—along the way to ultimate disposal. You may also supply the ultimate disposal for the system too. Relatively few companies provide the entire system that I have just described.

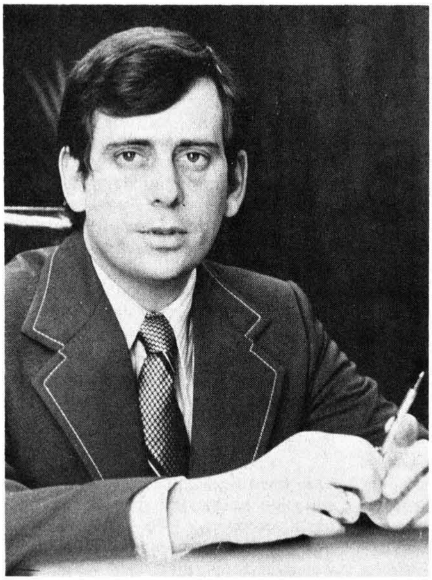
How does the company stack up against other so-called solid-waste agglomerates? Waste Management in its current form as a national, publicly held company is about two years old. With respect to other companies in the field, in terms of total sales in solid waste management, Waste Management, Inc., would be the second largest firm but very close to the number one firm, Browning-Ferris (BFI). I would estimate that SCA would be number three, Sanitas would be number four, Mobile Waste would be number five, and Waste Resources would be number six. In terms of markets served, Waste Management is in 47 markets at the present time.

How does your management philosophy set you apart from other solid waste agglomerates? I think there are certain aspects which make Waste Management similar to other companies, and there are certain aspects of our management philosophy which do separate us. The executive group of Waste Management has been predominantly involved in the waste management field. For the past six years, before joining Waste Management, I was involved with the industry-wide problems of this industry, as the executive director of National Solid Wastes Management Association (NSWMA). The other officers of this company have been primarily involved with waste management through almost all, and in many cases, all of their careers. Our vice-president for operations, Phil Rooney, worked with board chairman Dean Buntrock before we were a public company. He worked his way through college working in the solid waste field right in operations. Another vice-president, Larry Beck, who is also a member of our executive committee began with one truck and built his own very successful company. Dean Buntrock and Wayne Huizenga much the same. Our financial vice-president, as well as our treasurer and controller both, was with Arthur Anderson before joining Waste Management, but even there, a substantial portion of their time was in the service of leading waste management companies. Our people have been steeped in perspective in the waste management field. And it clearly has reflected itself in operations and in our performance.

ORGANIZATION

What is the organization of the company like? We are organized at a division level, a group level, and we decentralize management to the greatest possible extent in the various regions throughout the country. This, the Midwest, is one of the largest waste management regions. Florida and the Southeast represent an important growing region for the company. The western region is one that we are devoting a great deal of attention to right now.

But in addition to that type of geographical stratification, the company also has at the corporate level a management services group and an engineering services group. We have a centralized computer system that is available to serve all of our systems. So while we try to decentralize organization by vesting the greatest possible degree of decision making at the operational level, we have a corporate operational and financial control system that we think is second to none in the industry. And we



At his command position, Harold Gershowitz is president of Waste Management, Inc., the second largest solid waste management company in the United States. The company's top administrative executive tells ES&T's Marty Malin how recent growth has strengthened the company's position in the field and how many of the new concepts that he (Gershowitz) fought for in his former position as executive director of the National Solid Wastes Management Association are now becoming a reality. Waste Management is trying hard to lead the field in performance; sales have soared since the company went public two years ago.

provide an entire panoply of corporate services, be it management service, safety, insurance, or engineering from the corporate level. We have a large, and again we think a very effective, marketing department headed up by our vice-president in marketing, John Melk, whose department has been responsible for the development of all of the markets Waste Management has entered in the past couple of years.

ACQUISITIONS

The company seems to be pursuing a course of vigorous acquisition—you bought something like 42 companies in the first three quarters of 1972. How long will this fast clip continue? The acquisition pace in the future will probably not be nearly so rapid as it has been in the past. Our acquisition program has been an important part of our growth program. This has been a goal-oriented program to allow us to establish centers of capability in major markets throughout the country. This industry, just four or five years ago, was under a tremendous amount of pressure and criticism from agencies in Government—environmental agencies, from study groups who studied the field—because of its fragmentation, because there appeared, just a few years ago. to be no company in the country who could respond to problem-solving needs on a national basis. It would have taken decades for a company to begin from scratch developing such a capability throughout the U.S. The problems of recovery and the problems of waste management have been such that I don't think the country or the Government or anybody else would have waited for that type of industry to emerge, so Waste Management and other companies in the field have developed a national capability by affiliating with others through a well-planned acquisition process.

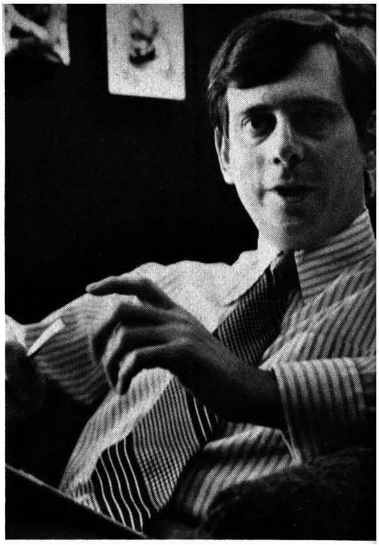
What do you look for when you want to acquire a company? Essentially, we do two things. First, we totally survey the market. We've surveyed the entire country and we have teams of people who do nothing but survey markets throughout the United States. When we think that we see a company that would be compatible with Waste Manaagement, a company that's operational philosophy seems to be similar to Waste Management's, we then request permission to do both a financial review and an operational review of that company. The management is extremely important to us. We've looked for young management, for young people who are dedicated to this field.

Second, we've concentrated to the greatest extent possible on those markets that are growing at better than the national average. There are markets in the country that are growing at 7, 8, 10%, some 12, even 18%. We've looked for markets that offer a great deal of new opportunity with expanding industry and commerce, rather than those markets that we refer to as mature markets that have shown no growth opportunities.

When you stop growing by acquisition, what lies ahead, say, in the next decade? As for the future, I think that we look to the areas of processing and disposal. We think that there are vast areas of new business opportunity in disposal, and our own experiences indicate that this is an area which is developing rapidly. More and more public agencies are looking to private enterprise to solve their disposal problems, as well as their collection problems. The areas of civil systems, or what we have in the past called special projects—such as our incinerator conversion projects, our solid waste reduction center in Pompano-Florida, the milling process, rail haul projects, our special projects in recovery such as our paper activities, and clearly the opportunity in liquid waste disposal, to which we've also made an important commitment—really represent astronomical potential for future growth for our company. Unparalleled, I think, in American business today. And I think that those will be the battlegrounds on which competition will continue to play a significant role.

Do you look upon any one geographical section of the country as your preferred hunting grounds or, to put it more directly, would you raid the henhouse in Texas, near BFI territory? We're in 19 states and we have municipal contracts with nearly 80 municipalities throughout the U.S. Waste Management will go and operate in any market that its management considers representative of new opportunity. There will be no area of the country that represents opportunity in which we're not going to be involved.

You have interests in Canada. Do you plan to become a truly international company? We have an extremely fine operation in Toronto. I would imagine that it is about the largest, industrial-commercial waste management company in North America. We also are active in Calgary. And I would anticipate that there will be other opportunities in Canada to which we will be responsive. Our marketing department is also studying the opportunities in Europe. As a corporate philosophy we're going to know as much as we can about any opportunity in the waste management field anywhere that opportunity might be.



"There will be no area of the country that represents opportunity in which we're not going to be involved."

—Waste Management's Gershowitz

SEGMENTS

How does the municipal segment of your business compare with the industrial segment? We have a semantics problem. When you speak of municipal waste, if you're referring to household or domestic waste, we have literally hundreds of thousands of such customers but most of Waste Management's business in terms of its revenue, is in the industrial and commercial area. We represent three quarters of a million customers, about 70,000 of whom are industrial and commercial customers. The balance would be households throughout the country, although the industrial and commercial business would represent about 80% of our total business.

There are many local companies which will only do residential collection. The opportunities to be innovative have been greater in the industrial and commercial area than in the residential area. The development of containerization systems and stationary compaction and so on has been particularly applicable to industrial and commercial installations. Industrial and commercial collection is clearly more capital intensive than is residential collection which is somewhat more labor intensive, although in the private sector, residential collection is far less labor intensive than it is in the public sector. Government studies have shown that in many municipal systems the cost of labor is as much as 85% of total cost. I'd say that it's much closer to 30% in a well-run private system. In industrial and commercial waste management, we can go to one-man totally automated collection systems with mechanized containerization systems and stationary compaction; you can just be more innovative at this point in time in the industrial commercial area.

We've been as innovative as I think current technology allows us to be in residential collection. I guess we're providing as much one-man residential collection service as anybody in the country. We've gone to total disposable containers or plastic bags systems. In one installation (Plantation, Fla.), we have a plastic bag system where the entire cost of collection and disposal is built into the price—the person pays for the bag and as a result of that you have somewhat of a user charge system. If a family throws away more waste, it needs more of those containers and pays proportionally more for the service.

What do the customers think of that? It's a very popular system. They like it and we like it. The system does a number of things, it makes people conscious of what they throw away and if they are a little more careful, they need fewer of those bags and can get the service for less. We've also experimented with resource recovery, we've provided certain bags in which they put, for instance, aluminum containers and we take those away free. That meant that all of that volume got out of the chargeable bag so we have provided a financial incentive to separate at the source. They buy these bags at their local store or service stations and when they buy the bag, they pay for their service so we have no city-wide billing system and no billing problem as a result of the system. It's highly imaginative and innovative and it has worked very well.

TECHNOLOGY

EPA's spending for solid waste management in fiscal 1973 has been drastically cut from the level in fiscal 1972. Some people have suggested that the cut reflects an administration view that new technology is not needed to solve the solid waste problems. How do you view those developments? Let me refrain from commenting on the size of the budget, because I don't exactly know what has gone into the planning of the budget. However, I think the direction shown by the Administration is essentially the proper one. I do believe that a huge federal funding program geared toward solid waste management operations throughout the country would be an absolute disaster. I think it would result in the funding of many of the least efficient systems and it would contribute to those inefficiencies. I think that to the extent the federal role is one of the environmental regulation, the Government would be making the greatest possible contribution.

At Waste Management, do you think of trash as "urban ore" or just plain trash? Some people have called trash "urban ore," and some people have called it a "resources out of place" and I think, to be perfectly candid with you, those terms are gross non sequiturs. Trash is trash until you can move it to the marketplace and do something with it, and in the absence of being able to do that, your primary obligation must be to move it to disposal and to ultimately dispose of the material as efficiently and in as environmentally sound a way as possible. We feel that there will be opportunity developing in resource recovery. And we have an entire department whose whole goal is to be responsive to those opportunities. But we think that it's terribly important that those moves be very well thought out and again be goal-oriented. Answers are not going to be found in some new black-box technology that allows us to do something with it that we can't do now. We know how to do with waste almost everything that has to be done. We can separate almost any fraction of the waste mix for which there is demand. The dialog is inventory-oriented, but the answers are demand-oriented. And in many cases, well-intentioned people have gone out and created great inventories without doing anything to stimulate a new demand for that material. What often happens when you do that, is that you successfully depress the value of that material in the secondary market and you have really done something that is quite counterproductive.

RESOURCE RECOVERY

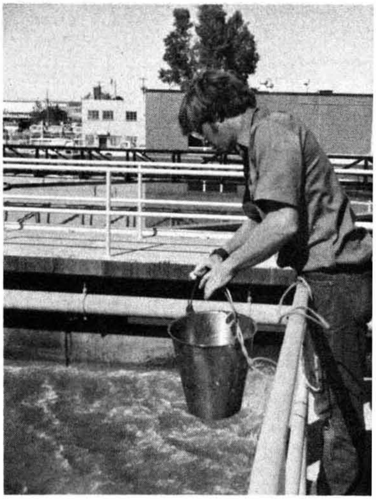
How do you see the outlook for recycled materials generally? We think that there can be and will be certain new opportunities in waste recovery, and Waste Management's goal will be to be responsive to those opportunities. We have some other projects on the drawing board but we think that it basically has been a disservice when people have oversimplified the task of resource recovery by implying that waste is an urban treasure. If it were an urban treasure, very little would be disposed of. There are going to have to be significant institutional changes and market changes—possibly changes in our entire tax structure—before it becomes feasible to recover vast quantities of waste beyond those quantities recovered now.

What about recovering energy from wastes? We think that in the area of energy conversion, vis-a-vis the St. Louis-Union Electric project, that we do see real opportunity. This is an area of recovery in which we have a great deal of interest, and we have people working specifically in this area. I don't want to indicate where or what we think our time frame is, but I am probably more optimistic about the future of energy conversion as it relates to resource recovery than I am about massive recycling of materials back into the waste stream. We are recycling significant quantities right now—we're reclaiming ferrous metals from our incinerator program here at Incinerator, Inc. in Illinois, and we have one of the largest paper operations (Lisner Paper Recover Div. of Waste Management) in the U.S., but these are recovery success stories that are exceptions. We've made them the exceptions and they just cannot be translated on a broad-scale basis to practical application throughout the U.S. The markets are not ready for that.

Just what should be the roles of government and private enterprise relative to solid waste management? I feel that a good waste management system represents an equation and both sides of that equation have to be satisfied. One side of the equation clearly requires the strongest practical environmental regulation and direction setting. Nobody can do that but government. I think the Federal Government has an obligation to develop those standards. They also have an obligation to make them practicable and workable.

EPA troubleshooters back up enforcement branch

National Field Investigation Centers in Cincinnati and Denver send out investigative teams before the agency takes legal action



Investigation. *NFIC technician hand-samples influent as it enters a waste water treatment plant (above). NFIC-Denver recently moved into a new office and laboratory complex (right)*

Ever wonder how EPA obtains evidence for its legal actions and enforcement conferences, or forms a position on emergency situations such as the mercury scare a few years ago, or develops effluent guidelines based on best practicable technology? Well, special teams of EPA water pollution "trouble shooters" have been in action around the country for several years.

These pollution investigative teams are located at two National Field Investigation Centers (NFIC)—one in Cincinnati, Ohio, and the other in Denver, Colo. Each has about 75-80 personnel. The centers direct and conduct studies, surveys, and reports preparatory to enforcement actions taken by EPA; participate in developing effluent limitations; direct and assemble technical support required for legal actions; and provide expert witnesses at hearings in connection with permits.

NFIC-Cincinnati, headed by A. D. Sidio, has been around since 1961. It was formed as a team of investigative experts under the U.S. Public Health Service and was continued under the Federal Water Quality Administration and functioned in response to enforcement proceedings of the governing agency.

In July 1970, NFIC-Denver was created. Tom Gallagher, formerly head of engineering services in EPA's Southeast Water Laboratory, was named director of the Denver operation. Soon after EPA was officially sanctioned in December 1970, Administrator William Ruckelshaus recognized the "need to develop facts as soon as possible if we are to take effective enforcement action against polluters" and relied heavily upon the two centers.

Both centers report directly to Murray Stein, EPA's chief enforcement officer in the enforcement proceedings division. Through Stein and the deputy assistant administrator for water enforcement, the centers are under the auspices of John Quarles, assistant administrator for enforcement and general counsel.

Official mandates

Each NFIC has three major functions. First, NFIC personnel are to be available as a major task force as emergency situations arise. For example, in the environmental mercury episode, NFIC-Cincinnati coordinated testing for mercury between regions, cooperated with U.S. Geological Survey scientists working on the same problem, and negotiated controls with the chlor-alkali industries.

Second, NFIC provides large-scale technical support for short-term major problems that are beyond EPA regional resources—requiring excessive amounts of money or large numbers of personnel to handle the situation. At the request of EPA headquarters and its Region VI, NFIC-Denver surveyed the Houston Ship Channel to determine the nature and characteristics of wastes—toxic substances, heavy metals, etc.—discharged into the Channel and Galveston Bay. The final report contained the environmental effects of the discharges and recommendations to meet water quality standards which led to the Galveston Bay Enforcement Conference.

Last, but not least, NFIC provides nonroutine specialty services to EPA headquarters and regions that, by reason of their daily duties, the offices would not be inclined to do themselves. For example, NFIC was given the task of developing interim effluent guidelines for 25 standard industrial classifications. With sophisticated chemical analysis and industrial waste expertise, NFIC determined the best practicable control technology for each industry. From these interim guidelines, states can issue discharge permits without delay until final effluent standards are adopted. All samples taken during investigations or surveys are held in security storage, and NFIC personnel are on call until all legal action is resolved.

NFIC's Gallagher
"Move in and get out"

Expertise in many areas

Either one or both of the centers have special capabilities in several areas valuable for environmental monitoring. One such area is remote sensing. Through agreements with the U.S. Air Force (using F-11's in their training program) and with photo-interpretation expertise, NFIC-Denver can assess the physical effects of oil spills, algal growths, heat discharges, and septic water discharges on the aquatic environment. This center monitored heat discharges from power plants on Lake Michigan by remote sensing and also documented oil spills in the Houston Ship Channel for referral to the Justice Department.

Another NFIC speciality is industrial waste evaluation. From the NFIC-developed effluent guidelines as well as field investigations of hundreds of industrial sources, the Centers have accumulated a wealth of experience, data, analytical information, and education in practical problems of process control.

NFIC personnel are also knowledgeable in municipal waste treatment. NFIC-Cincinnati specializes in biological waste treatment, whereas the Denver office places emphasis on physical-chemical treatment developments and operations. The Centers have undertaken projects involving nitrogen removal at Sioux Falls, S.D., and improving settleability characteristics at Kansas City, Kan., among others.

The Centers use several environmental computer information systems that detail water quality effects from complex waste discharges and provide water quality inventory data. Through remote terminal hookups to computer systems in Washington, D.C., and Philadelphia, Pa., NFIC scientists have access to more than two million pieces of literature. As well as being connected to the STORET system (ES&T, February 1971, p 114), the Denver Center utilized a TOXICON file to support the Houston Ship Channel waste source survey to determine tolerable limits for complex organic discharges.

NFIC laboratories perform complex organic analysis with the best equipment on the market. The laboratories are among the most up-to-date in the country, featuring biology, microbiology, fish bioassay, autoanalysis, wet chemistry, tracer analysis, and quality assurance capabilities. Gas chromatographs–mass spectrophotometers are employed to analyze complex organics in waste discharges with respect to specific compounds in the discharges. The information is used to develop individual effluent limitations for the compounds involved. The organic wastes in the Houston Ship Channel were examined by this means.

In addition, the Denver Center has five mobile labs for extensive testing in the field—one for bioassay, two for chemical analysis, and two for microbiological analysis. NFIC-Denver has moved into a new building, just completed this month, containing 12,000 ft^2 of lab space and 18,000 ft^2 office space.

Each Center employs 75–80 persons including biologists, microbiologists, engineers, organic and inorganic chemists, hydrologists, lawyers, and administrators. When asked about the small number of people employed to perform this specialized work for EPA headquarters and all regions, Tom Gallagher, NFIC-Denver director, summed up the situation, "When we get a request with well-defined technical objectives, we move in fast, get the job done without sacrificing any quality of work, give them a report, and get out." In spite of being few in number, NFIC personnel complete a number of projects within record time.

What NFIC does

At present, NFIC is only mandated to operate in the water pollution control field since the procedures of enforcement in other environmental areas are not finalized. However, if the opportunity arose to investigate other pollutant sources, Gallagher explains, the matter would not be ignored. In fact, NFIC-Denver has been involved in situations covering both air and water pollution.

There's no real breakdown on the territories covered by the two investigation centers. The Center with particular expertise in a certain area will handle problems in that area. Generally, however, NFIC-Denver handles the five western EPA regions and the southeast region, and the Cincinnati office covers the others.

At press time, the Denver office had 22 ongoing projects; most will be completed in three to six months. Last year, NFIC-Denver undertook a 200-mile survey of the South Platte River and evaluated the waste discharges, climatic conditions, water quality, tributary quality, and recommended controls for waste discharges. Region VII requested the rundown on water quality in July 1971, and NFIC submitted the final report in March 1972.

A report on the Memphis, Tenn., area covering 22 large discharges and evaluating recommendations took only four months. Region VIII requested a report on the Denver, Colo., metropolitan area in preparation for negotiations with the city on what will be needed to meet water quality standards. NFIC covered the status of industry in the area, water sources, waste treatment, sampling, and made recommendations within six months.

When emergency situations arise, the team moves even faster. For instance, EPA wanted to take court action against Rohm & Haas located on the Houston Ship Channel because of the far-reaching effects of their discharges as shown by analysis in the regional lab. The investigators moved in, determined that Rohm & Haas wastes did reach shellfish areas, and were in court within two and one half weeks!

Two years ago, NFIC sampled areas in both Colorado and New Mexico when fish with a high mercury content were found in nearby Navaho Lake. At the requests of Regions VI and VIII, NFIC investigated four possibilities; application of mercury-containing fertilizer, erosion of rocks with a high mercury content, point source discharges, and aerial mercury discharges from the controversial Southwest power plant complex.

One project involves aerial reconnaissance over Lake Superior; here NFIC is working with EPA's Freshwater Laboratory at Duluth, Minn., to show the effects of the taconite tailings that Reserve Mining Co. is presently dumping into the lake. The results will be submitted to Stein and Quarles. CKL

With more than 80,000 municipal subdivisions
in 50 states, there is compelling reason
for decision making for a state's betterment

Congress: much ado about land use

The Number 1 environmental and long overdue issue in this legislative session of Congress is land use. It's not the first time that legislative proposals on land use have been taken up; in fact, it's the third time in three Congresses. After four days of hearings in the 91st and 10 days of hearings and Senate passage in the 92nd, the issue once again is before the legislators. One of this year's proposals, S. 268, is identical to the Senate version passed last session.

The whole purpose of S. 268 is to assist states in developing land use programs for critical areas and for land uses of more than local concern. The gut issue is to create a process whereby other than local jurisdictional decisions are made which, in the whole picture, would not be detrimental to a state's overall betterment.

Everyone agrees that the Federal Government should act as a catalyst in establishing such a process and in assisting states to face up to land use decisions. But the specifics—how, when, incentives, penalties—are largely unsettled at this time.

Generally, zoning is performed at the local level. But a real problem is the lack of participation at the state level in the overall state planning role. In view of this fact, a basic intent of the legislation is to encourage states to establish a process for identifying and controlling those major land use decisions which require a broader review than that provided by the current fragmented approval process at the local level. The magnitude of the problem becomes glaringly apparent with the realization that there are more than 80,000 different municipal subdivisions in the 50 states. And zoning in the past has, in many cases, been performed to the detriment of the state's overall development.

The emphasis, then, in the land use legislation is on major or significant land use decisions which tend to have regional impact. As a first cut, these decisions would include major airport and highway developments. Additionally, they would include the protection of critical environmental areas—flood plains, wetlands, timberlands, farmlands, and historic areas, to mention a few.

As long as the necessary decision-making processes are established at the state level, the Federal Government will not second-guess the land use decisions that result. But it is important to note that this land use legislation is not intended to be all inclusive, an umbrella piece of legislation. In fact, more specific legislation of the land use type would be in order for power plant siting and strip and underground mining.

Hearings

In a recent round of hearings held by the Senate Interior and Insular Affairs Committee, witness after witness pointed out that lack of a national land use policy results in an increasing threat not only to rural land but also to urban open spaces sought by real estate developers and land speculators.

CEQ chairman Russell Train said, "We have tended to take the land for granted, perhaps because of our frontier tradition. We need now to develop a sense of stewardship for the land." He continued, "The drained wetland, the flooded valley, the farmland that is subdivided or paved can never be restored in any practical sense. Thus, land use decisions tend to be permanent and thereby limit future options." He also pointed out that land use has been the subject of the President's annual environmental messages since 1971.

The land use proposals do not provide for federal control in land use decisions, nor is it intended to undermine state and local authority. At best, S. 268 is an act to require states to exercise states' rights. But differences of opinion center on how to nudge a state into doing something and identifying state-level problems and solutions.

For example, if a state fails to develop a land use plan within three years, then certain penalties or sanctions, as they are specified in the proposal, could be invoked by the Federal Government. Basically, in top land use priority items—highway and airport developments—states which do not attempt to control the growth which these facilities induce would receive less in federal funds with which to construct such developments than those states with a process to control growth. States that fail to adopt land use proposals would lose a graduated amount, from 7–21% of their federally supported highway trust funds, airport construction funds, and land and water conservation funds.

Judgment. *No minimum land use standard is possible; each depends on value judgment and aesthetic judgment*

The S. 268 legislation has been estimated to cost about $170 million in 5 years—$40 million for each of the first two years and $30 million for each of the remaining three. Some legislators question the effectiveness of $40 million divided by 50 states to begin the process. Others support incentives rather than the negative aspects of sanctions.

Sen. Jackson
". . . third time in 3 Congresses"

CEQ's Train
". . . needs the legislation now"

No official seems willing to suggest basic minimum standards for land use planning similar to the standards for air and water pollution control. CEQ's Train pointed out that a standard could not be set due to the value and aesthetic judgments needed in each land use decision.

State activity

Land use experiences in the states vary; all states are aware of the problem of land use planning and decision making, but only a handful have done anything on a state-wide basis. Planning initiatives are under way in Colorado, Florida, Hawaii, and Vermont, and another few states—California, Delaware, and Massachusetts—have legislation on particular areas such as coastal regions. Iowa has adopted erosion control standards which might serve as the model for other states with flood plains.

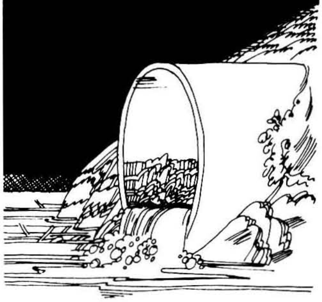
However, development pressures are occurring in all states. In Maryland, for example, an estimated 30,000 acres of agricultural land are lost each year to real estate development and speculation. Consequently, during the three years that the land use legislative proposal has languished in Congress, more than 90,000 acres of land in Maryland alone have been lost to development. There is yet another way to look at the same problem. The air pollution problem in Los Angeles today is a consequence of land use decisions made years ago.

If this legislative proposal is enacted, states would be required to reassert their inherent constitutional authority to review and override, if necessary, local decisions which have an impact beyond the local jurisdictions. This process, a key item in the Senate proposal, would give a state regional benefits as new communities are added and lands are developed.

Fundamentally, the legislative questions on land use are similar to the nagging ones on solid waste—namely, at what level should the Federal Government get into the problem? Considering the fact that only a handful of states have enacted state-wide planning authorities, we note that the Senate bill would at least prod states into planning future development. But whether two years should be spent in the planning process, before moving ahead with sanctions, is moot. On the other hand, the Administration wants not just planning, coordination, or information gathering, but aims to put teeth in the planning process—not just more plans—hence the endorsement of sanctions.

As we move ahead on land use, certain reports hopefully will shed more light on the issue. CEQ soon will be releasing its report on the constitutional limits of land use control. CEQ and HUD jointly contracted for a nation-wide study to assess the current phenomena of recreational land sales and leisure home development.

What will emerge in the way of improved land use legislation is far from clear at this time. There is no question but that the country needs this legislation now. Every day is another threat to limited land resources and loss of precious land to real estate development and speculation. But the dichotomy of view indicates that more time will be spent before legislation is passed. SSM



First lesson in resource recovery

Shredders are being used more and more to yield a homogeneous, manageable material from mixed municipal solid waste

If and when this country takes resource recovery seriously, then shredding will become a household word. No matter what else is planned in whatever scheme you happen to be looking at, shred you must. Every other step comes later.

"Shredding is a preprocessing technique to a final solid waste disposal method," explains Greg Devejian, Solid Waste Systems, Eidal International Corp. (Albuquerque, N.M.), one of a number of firms in the business. ES&T visited Eidal International Corp., a subsidiary of Southwest Factories, Inc., which has more shredders in service than any other manufacturer and is presently number one in shredder sales for municipal solid waste applications.

In 1961, Roy Eidal, the firm's founder, marketed a shredder for reclaiming steel from automobile bodies. He later expanded his shredder line for application to solid waste. Eidal's shredders range from the small 100-hp model that grinds small tonnages to intermediate 400–1000-hp machines that handle 20–70 tons /hr of solid waste to the giant 2000-hp shredders that can chew up an auto every two minutes.

It's true; shredding—the dry liberation, size reduction, and homogenization of solid waste—is used in more and more areas prior to municipal refuse disposal. Shredding encompasses a variety of techniques to grind solid objects such as impacting, tearing, and shearing. Different shredder manufacturers promote the various forms of reduction.

Advantages of shredding

Shredding municipal refuse has several inherent advantages regardless of the ultimate method of disposal. For example, if solid waste is to be landfilled, shredding can reduce operating costs, extend landfill life, and diminish problems. By reducing the volume of the waste by 50–70%, shredding produces a denser, more compact material to landfill. Therefore, hauling costs are lowered, and land costs are reduced as landfill life is extended. Unshredded refuse has a density of 300–400 lb/yd^3 while shredding can increase the density to 700–800 lb/yd^3 (depending upon the moisture content).

Furthermore, shredded refuse may eliminate the need for a daily cover of soil on landfills, which accounts for an estimated 10–20% of available landfill space. Demonstration tests at Madison, Wis., aimed at determining the effects of shredded refuse in an uncovered landfill, revealed that shredded solid waste does not need daily cover, does not blow in the wind, does not burn easily, does not attract vermin and flies, and has little odor.

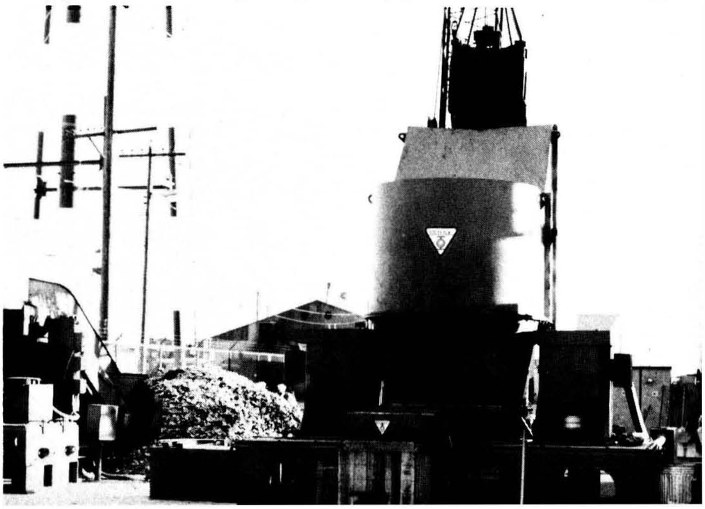
If refuse is to be incinerated for steam or electricity, the process usually consists of suspension burning which requires controlled particle size. The same is true for pyrolysis.

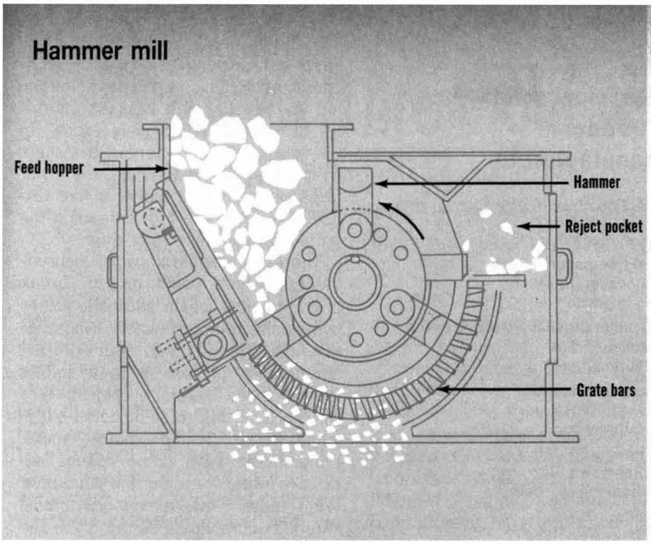
The most important area for shredding is resource recovery. Shredding produces homogeneous particles from which glass, paper, and metals can be extracted for reuse, and the remaining organic refuse can be more effectively incinerated for energy conversion. The particle feed must not exceed a certain size so that equipment can be designed to separate it. Also, liberation of composite materials is necessary; some items, such as paper, may cling to other objects and block the separation system.

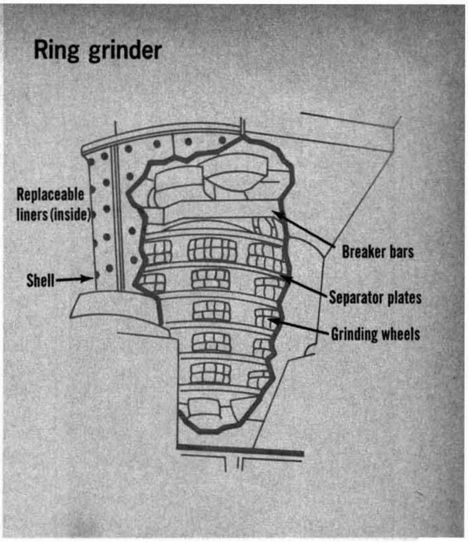
Shredder categories

Approximately 50 companies are in the shredder business; basically, there are four different application areas of shredding: process grinding, municipal solid waste, metal processing, and industrial applications. Process grinding equipment, for such as mining operations and pulverizing or crushing rock, is manfactured by about 35 companies. About 10 firms are in the solid waste field and perhaps other application areas as well. The remaining five companies produce extremely large machines (in the neighborhood of 6000 hp) for steel and metal processing. Then there are industrial specialty applications. For example, scrap papers from the desks of executives may be shredded prior to disposal, or defective or experimental machinery may be shredded to protect patents.

Ring grinder. *Cast as a single unit, Eidal's equipment needs little maintenance*







Equipment types

All shredders are brute force machines with motor-driven rotors to tear up waste materials introduced into them. However, shredders on the market today can be loosely grouped into three basic types. First, the tooth roll crusher operates on the principle of force of impact to crush. A horizontal rotor with teeth hurls objects against a steel breaker bar which causes the material to shatter.

As a general rule, the tooth roll crusher is used for coarse crushing; it reduces bulky items (refrigerators, bedsprings, etc.) to 12-in.^{2} pieces. Since there is no particle size control, the discharged pieces are too large for incineration or pyrolysis. The machine does not have a "tramp" (usually unshreddable metal, such as anvils) material rejection system, but large unshreddable objects will pass through the machine. The National Center for Resource Recovery (Washington, D.C.) is studying this machine for use in solid waste recovery systems, but views it as a less likely candidate under those operating conditions and scale. The East Side incinerator in Buffalo, N.Y., uses a tooth roll crusher manufactured by Hazemag USA, Inc. (Uniontown, Pa.), in its municipal solid waste operation.

The second type of shredder is the more familiar hammer mill which is a horizontal rotor machine with flailing hammers attached. Swinging hammers impact the refuse against breaker bars mounted on the upper half of the hammer mill. Refuse is ultimately swept to the lower section of the crusher and pounded through grating. Larger pieces are swept around and around until they will pass through the grate. Tramp iron is either swept into a trap or will pass through the system. Several U.S. installations employ hammer mills in their municipal solid waste operations (box).

Typical shredder installations

Alabama, Mobile
Gruendler—Composting operations; now closed

California, Los Gatos
Pennsylvania Crusher—Operating at 30 t/hr since 1970

California, San Diego
Williams—Used prior to baling and landfilling

Connecticut, Milford
Eidal—Operating since 1972

Delaware, New Castle County
Gruendler—Operating 1972

Florida, Pompano Beach
Heil/Tollemach—Operating 1972

Georgia, DeKalb County
Eidal and *Heil/Tollemach*—Operational early 1973

Kentucky, Louisville
Williams—Intermittent operation over last few years

Missouri, St. Louis
Gruendler—Operating 1972

New York, Brooklyn
Pennsylvania Crusher—Operating since 1971 for composting

New York, Onondaga County
Eidal—Scheduled for operation last month

North Carolina, Guilford County
Eidal—Scheduled for operation this year

Rhode Island, Providence
Eidal—Operating 1972 for composting

Texas, Houston
Williams—Intermittent operation

Washington, Vancouver
Eidal—Operating for landfill

Wisconsin, Madison
Heil/Tollemach—Operating since 1967

Source: National Center for Resource Recovery

The third category of crushers are vertical rotor shredders. The patented vertical ring grinder is manufactured by Eidal International. Instead of flailing hammers, it has nonweldable cast grinding rings attached to the rotor. As refuse enters the machine, a rotating breaker bar at the mouth of the barrel first impacts the bulkier objects into small pieces. The waste then drops into the tapered barrel by gravity and the force of more material added on top. The refuse is subjected to a grinding, shredding, and tearing action in the barrel caused by free floating grinding rings attached to the rotor.

A choke ring at the bottom of the barrel limits the particle sizes passing through. The small (less than 3 in.) particles are then discharged from the bottom collection area by rotating sweeper blades. Tramp metal may pass through the shredder, but Eidal officials recommend removing such items from the waste entering the shredder.

The vertical rotor impacts no dynamic loading to the foundation which therefore does not have to be protected from pounding. Also, Eidal officials find that dust control equipment is not necessary if 3-5 gpm water is sprayed on the municipal refuse entering the shredder.

Another version of the vertical rotor shredder is the vertical hammer mill produced by Heil Co. (Milwaukee, Wis.). It has hammers on the rotor instead of rings. Refuse enters a prebreaking chamber for initial impact and breaking, and then passes into the grinding chamber containing

Municipal solid waste shredder manufacturers

American Pulverizing Co.
St. Louis, Mo.
Hammer mill

Eidal International Corp.
Albuquerque, N.M.
Ring grinder

Gruendler Crusher & Pulverizer Co.
St. Louis, Mo.
Hammer mill

Hammermills, Inc.
Cedar Rapids, Iowa
Hammer mill

Hazmag USA, Inc.
Uniontown, Pa.
Tooth roll crusher

Heil Co.
Milwaukee, Wis.
Vertical hammer mill

Jeffrey Manufacturing Co.
Columbus, Ohio
Hammer mill

Longhorn Construction Co., Inc.
Sulphur Springs, Tex.
Horizontal flail mill

Pennsylvania Crusher Corp.
Broomall, Pa.
Hammer mill

Williams Patent Crusher & Pulverizer Co.
St. Louis, Mo.
Hammer mill

Source: National Center for Resource Recovery.

the flailing hammers. Neck rings hold the refuse in the chamber until the particles are small enough to pass through for discharge. The narrow neck between the prebreaking and grinding chambers serves as a rejection system for tramp metal which is discharged from a point on the side of the machine.

Shredder characteristics

There are other differences between the pieces of shredding equipment other than construction. The first is wear and operating costs. In the hammer mills, the hardened steel hammers are welded onto the rotor of the machine and frequently need to be replaced. In contrast, the vertical ring grinder is cast as a single unit and is replaced infrequently, according to Eidal spokesmen.

Sizing is handled differently in the machines also. The tooth roll crusher has no control over sizing; a hammer mill pounds the material through grates; and the ring grinder literally grinds the material before it passes through a choke ring.

All shredders are only as good as the conveyers that feed and discharge them; all need to be conveyer-fed for best results. In the horizontal machines, refuse is generally fed into the top side, and the majority of the impacting is done in 25–40% of the periphery of the shell. In the vertical machines, the rotor turns on a vertical plane as the refuse is fed into the top, spreading the force over the entire rotor area.

There are certain known "unshreddables" which could foul or break any municipal waste shredder if they bypass the rejector system. Rugs, for example, may come out of the shredder in pieces up to a square foot in size; sheets of plastic may wrap around the rotor or come out in long strips. Tramp metal—anvils, crankshafts, steel cable—cause excessive wear or clog the shredder. With these few exceptions, most shredder companies, when given the characteristics of the waste and specifications to be followed (such as particle size and speed) can produce the machines to handle the job.

Applications

A number of shredder installations are operating in the U.S., and shredding is a required prerequisite to many undertakings. In Combustion Power's (Melo Park, Calif.) fluidized bed incinerator that burns refuse in a bed of aerated sand, all incoming material must be shredded. The National Center for Resource Recovery includes shredding in all its recovery schemes and emphasizes its importance for the upcoming National Resource Recovery Network (ES&T, December, 1972, p 1078). Last year, a $1.9 million shredding operation began in Milford, Conn. The shredder was built on the existing Milford landfill site, which was nearing the end of its useful life. With shredding, however, no new land was required for the landfill which serves 52,000 people.

Shredders can be used to grind up batteries to recover the lead or crush steel or aluminum cans for recycling. A distributor for Coors Inc. in California recently purchased an Eidal shredder package for use in aluminum can recycling.

Shredder costs vary depending upon the size and capacity of the unit. A San Diego, Calif., shredder that grinds refuse prior to baling had a price tag of $600,000; the Milford, Conn., unit cost almost $2 million. As a rule of thumb, a typical 50 tons/hr shredder will cost approximately $150,000, exclusive of installation and feed conveyer outlays. Operating costs run from $2–5/ton. Shredders have been around for years and may just be the ecological and economical place to begin to tackle the solid waste problem. CKL

Project Threshold verifies tests

Preliminary results from Phase One indicate all the tests are good and some are better than hoped for

The first results of Project Threshold—the three-year, \$2.25 million cooperative testing venture of the American Society for Testing and Materials (ASTM) to measure the validity of air pollution tests—are in and the project coordinators are more than pleased with the results. Although the raw data have yet to undergo final "polishing," and statistical treatment, indications are that the data are "very, very good," says Benjamin Levadie, chairman of ASTM's Committee D-22, the committee responsible for the project.

Project Threshold is now more than a year old (ES&T, January 19 p 23). Phase One, designed to validate several manual methods for testing ambient air quality has been completed; Phase Two is now under way and will focus on methods for stack sampling. Phases Three and Four, to be completed by the end of 1974, will test instrumental methods for both ambient and stack monitoring.

Phase One

The first phase of Project Threshold was designed to check accuracy and precision of six standard measurement methods published by ASTM for ambient air quality, according to Walter Cropper, project manager for Threshold. The tests validated in Phase One were ASTM methods D1607 for nitrogen dioxide in the atmosphere by the Griess-Saltzman reaction, D2914 for sulfur dioxide in the atmosphere by the West-Gaeke reaction, D2010 for sulfation rate by the lead peroxide candle technique, D1739 for atmospheric particulate matter by the dustfall bucket technique, D1704 for atmospheric particulate matter by the tape sampler method, and D3112 for atmospheric lead.

The preliminary data indicate that most of the tests are excellent when applied to the parameters for which they were originally intended, according to Levadie. In particular, two of the tests, "the dear, sweet, little dustfall bucket and the simple sulfation candle, have come out smelling like the sweetest roses possible," Levadie says.

The unpolished data, which suggest the validity of the tests although actual values may possibly be revised, show the following:

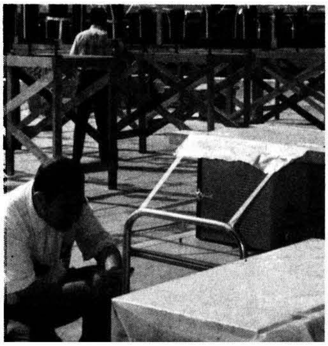
- D1607 (nitrogen dioxide). Based on 680 observations in the 5–400 $\mu g/m^3$ range, the test is generally reproducible and accurate. The standard deviation between duplicate samples tested by a single laboratory was about 2.7% of the amount present and standard deviation between laboratories was about 7.1% of the amount present. The smallest concentration of NO_2 that could be differentiated from zero as the mean of two values reported by different laboratories was about 8 $\mu g/m^3$ and about 4 $\mu g/m^3$ as the mean of duplicate results reported by a single laboratory.

At the ambient air quality level of 100 $\mu g/m^3$ set by EPA, the estimated standard deviation for reproducibility is about 13 $\mu g/m^3$ and the repeatability is about 5 $\mu g/m^3$.

Threshold data show that the values are slightly high when there is more NO than NO_2 in the air, but project coordinators claim that the ASTM's Griess-Saltzman method is still more accurate than the Jacobs-Hochheiser reference method prescribed by EPA (ES&T, October 1972, p 890).

- D2914 (sulfur dioxide). Based on nearly 700 observations with concentrations ranging from 5–400 $\mu g/m^3$, the West-Gaeke method tested by Threshold is accurate and more precise than the method promulgated by EPA which is based on a similar colorimetric reaction, according to data from Threshold teams. Standard deviation for repeatability is about 5% of the amount present and standard deviation from different laboratories is about 9.3%. The amount that can be differentiated from zero as the mean of values by two laboratories is about 8 $\mu g/m^3$ and about 5 $\mu g/m^3$ as the mean of duplicate results by a single laboratory. At the ambient air quality level of 60 $\mu g/m^3$ set by EPA, standard deviation of reproducibility was about 11 $\mu g/m^3$ and of repeatability about 5 $\mu g/m^3$.

Bucket brigade. *Threshold gives dustfall method high marks*



The Threshold team reports the standard deviations of ASTM's method, while determined at lower concentrations than those of an EPA-funded test of the reference method conducted by the Southwest Research Institute, were lower than those of the reference method.

- D2010 (sulfation rate). In about 85 observations with concentrations ranging from 1–50 $\mu g/cm^2$ day, both between- and within-laboratory standard deviations were about 6%. The smallest amount that could be reliably distinguished from zero was about 2 $\mu g/cm^2$ day. ASTM found the method to be free of bias.
- D1739 (particulate matter—dustfall). About 90 observations in the range of 1–50 g/m^2 month showed that between-laboratory standard deviation is independent of concentration and is about 2.3 g/m^2 month while the figure for within-laboratory tests is 1.6 g/m^2 month. The lowest value that could be reliably distinguished from zero is about 4.5 g/m^2 month. This method is also unbiased, according to ASTM.
- D1704 (particulate matter-tape sampler). About 500 observations in the range of 0.3–11 coefficient-of-haze (COH) units had a large standard deviation of reproducibility between laboratories. Within-laboratory variability or bias of the test was not studied, but the method and apparatus respond to changes as small as 0.3 COH, according to the Threshold data.
- D3112 (lead). Data collected ranged from about 0.06–6.0 $\mu g/m^3$ with the scatter of results between laboratories being a little less than 20% of the average amount measured. The method gives results that are about 20% higher than actual values, based on samples to which known quantities of lead have been added. The lead method is so sensitive that it can detect one lead-bearing particle/m^3 of air. No federal standard has yet been set for airborne lead. HMM

Magnesium carbonate flocculation with regeneration
of lime and coagulant is under full-scale investigation
in Montgomery, Ala., after successful pilot runs

Recyclable coagulants look promising for drinking water treatment

For the last half century or so, drinking water has been purified by roughly the same methods centering around alum or iron coagulation. The gelatinous nature of the hydrolysis products of aluminum or iron salts has served very well to trap floating solids and make possible their removal from water.

But the same gelatinous properties have made it difficult to dewater the sludges left over from water treatment. A newly developed water treatment process, developed by A. P. Black, professor emeritus of chemistry and environmental engineering at the University of Florida (Gainesville), and Cliff Thompson, a partner in the Montgomery, Ala.-based environmental consulting firm of Thompson and Tuggle, could change all that. Demonstrated under contract to the Environmental Protection Agency, the process uses magnesium carbonate as the coagulant. What makes the magnesium salt so highly attractive is that it's recyclable. Magnesium treatment also promises better quality water and easier sludge handling, although under current practices, magnesium carbonate coagulation costs more than conventional lime-alum or iron systems.

Developmental work

The process is the outgrowth of work done earlier by Black with softening plant carbonate sludge at Dayton, Ohio. Thompson, who recently received his Ph.D. under Black's direction, is now in charge of a full-scale test of the process at the 20-million gpd Clarence T. Perry water purification plant, just outside Montgomery, Ala.

The team carried out tests on natural and synthetic waters—water samples prepared by adding known amounts of contaminants to distilled water—in small jar tests and large 55-gal drum tests to work out the chemistry of precipitation before putting the process on stream at a 50-gpm pilot plant at Montgomery.

They finished the developmental work and began operation of the Perry plant in June of 1971. Within a couple of months, the evaluation phase of the work will be complete. EPA officials held a preliminary technology transfer meeting at the Perry plant in February.

The basic chemistry of the purification process is relatively simple. A lime slurry is added to raw water which contains either naturally occurring magnesium bicarbonate or magnesium carbonate which has been added. The addition precipitates magnesium hydroxide and calcium carbonate. The magnesium hydroxide acts in a manner similar to the hydrolysis products of iron or aluminum salts and forms a floc which settles impurities out of the water.

In essence, the treatment system is a combination softening and purification process. Softening takes place by raising the pH of water by adding lime to convert all carbon dioxide and bicarbonate alkalinity to the carbonate form according to the reactions:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

In the case of magnesium salts, the carbonate is converted to the hydroxide form by adding more lime:

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3$$

When magnesium is present as noncarbonate hardness, calcium is exchanged for magnesium and there is no change in the total hardness:

$$Mg^{2+} + SO_4{}^{2-} + Ca(OH)_2 \rightarrow Mg(OH_2) + Ca^{2+} + SO_4{}^{2-}$$

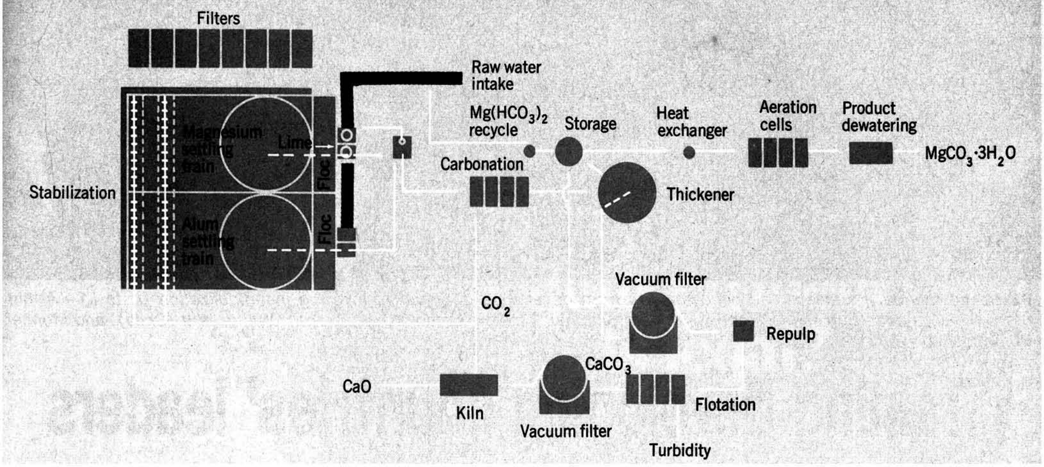
Reclaiming magnesium

Once the settled sludge is removed from the process, it may be dewatered and landfilled—a practice followed with conventional sludges. But with magnesium as the coagulant, it's possible to do more. The sludge can be carbonated by bubbling carbon dioxide through it, which solubilizes the magnesium selectively as magnesium bicarbonate. The magnesium bicarbonate can then be reclaimed from the filtrate obtained by vacuum dewatering and returned to the process. The filter cake, consisting chiefly of clay and $CaCO_3$, may then be landfilled or treated one step further. The lime values can be reclaimed from the sludge, and the carbon dioxide given off from the calcining of $CaCO_3$ to produce CaO for lime makeup can be used in the recarbonation process. At the same time, reclaiming the lime values further reduces the amount of sludge that must be landfilled. The sludge that's finally left is almost entirely clay—easily handled and environmentally stable.

The magnesium salt favored in the water treatment process is the carbonate trihydrate ($MgCO_3 \cdot 3H_2O$) form. As the trihydrate, magnesium carbonate does not add to the total dissolved solids content of the water.

Unfortunately, the salt is not commercially available since there are presently no large industrial uses for it. But the trihydrate could very well be available in sufficient quantities

Flow scheme of Perry Plant comparing $MgCO_3$ and alum processes



from cities which operate large-scale softening plants.

Cities which must treat water with relatively high magnesium content—including major metropolitan areas such as Chicago, Detroit, Cleveland, Washington, Indianapolis, Philadelphia, and Pittsburgh—would be able to recover large quantities of magnesium carbonate trihydrate which they could sell to offset the cost of water treatment. Thompson and Black estimate that about 150,000 tons per year of magnesium carbonate trihydrate would be produced by 20 cities with high magnesium water. By switching to the recycled magnesium carbonate process, these cities would not only be able to reduce their treatment costs, but would solve their present sludge disposal problems as well.

There are many advantages to magnesium carbonate treatment, Thompson points out. The magnesium carbonate system is at least as effective as iron or aluminum in removing turbidity and organic color from surface waters. Neither the base exchange capacity of turbidity causing clays nor the level of turbidity present significantly affects optimum coagulant dosage.

Unlike the gelatinous, ephemeral flocs formed with aluminum or iron salts, the magnesium hydroxide flocs are better formed and heavier since they are loaded with calcium carbonate. There is, therefore, more rapid and complete settling with less carryover of the floc in succeeding stages of water treatment.

The process carries a natural disinfection bonus with it. With alum and ferric sulfate treatment, viruses are removed to a certain extent by coagulation but can be recovered live from the floc. Because the pH of the magnesium carbonate system is so high, however (11.0–11.5), the viruses are not only removed by the flocculation step, but are destroyed by the alkalinity. Bacteria are also removed by the process, eliminating the need for rechlorination in many applications.

The high pH also promotes removal of virtually all the iron or manganese that may be present in some surface waters.

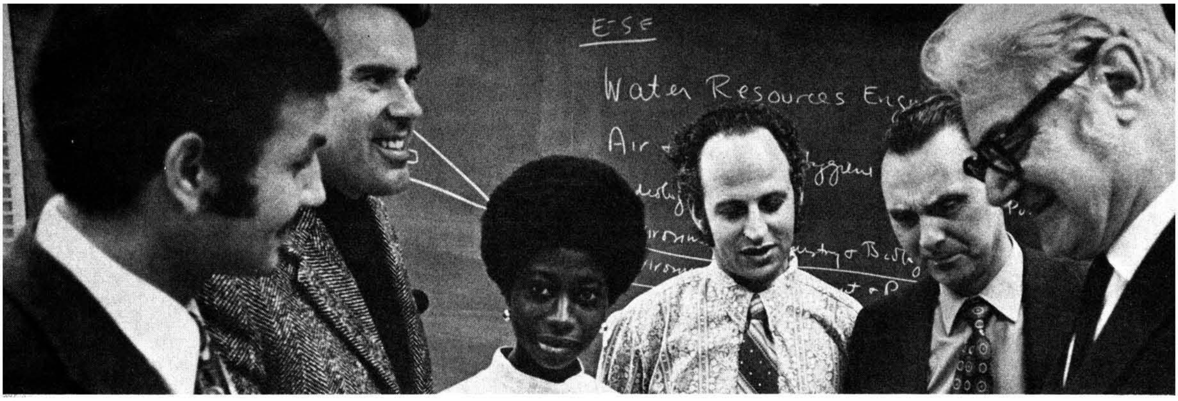
In operation

The magnesium carbonate process is in full-scale operation today at the Perry plant and residents of Montgomery have been drinking water purified by the process for about 9 months. The Perry plant is the ideal proving ground for the process since the plant consists of two parallel 10-million gpd purification trains, one of which uses conventional lime-alum treatment while the other uses the magnesium carbonate process. Much of Montgomery's water comes from wells and the plant is seldom run at peak capacity, but magnesium carbonate has been used on a large enough scale here to prove that it works reliably in day-to-day operation.

The Perry plant does not necessarily plan to convert to the $MgCO_3$ process, however, even when all the bugs have been worked out, Thompson says. The final utility of the process may depend more on federal regulations than anything else. For all its advantages. the magnesium carbonate process is more expensive than conventional treatment, in the Montgomery application—unless the cost of sludge disposal is fully accounted for. And much depends upon regulations for sludge treatment which the EPA may adopt.

While the process allows recovery and reuse of both lime and magnesium carbonate, Black and Thompson estimate that there are more than 4000 water plants in the United States that will not find lime recovery possible because of the small amounts of lime required at those plants. The carbon dioxide produced by recalcining figures high in total costs, however, since bottled CO_2 can come high. For plants that could not afford to make their own CO_2 for the recarbonation step, Thompson suggests that an alternative source of CO_2 might be found. Carbon dioxide could come from a diesel fuel or natural gas-burning engine, he suggests, or even from power plant stack gases or other industrial source.

The cost differences between the magnesium carbonate and lime-alum systems may be more apparent than real, Thompson says. For example, at the Perry plant, the cost of lime-alum treatment, without provision for sludge handling, is \$8–10/million gal. The cost for magnesium carbonate treatment, with purchased CO_2, high calcium lime, and purchased $MgCO_3$, without recycling of lime is about \$19/million gal. If dolomitic lime could be used and could serve as a magnesium source, the costs would come down to about \$12/million gal. If a CO_2 source—say from a diesel engine or power generating plant could be incorporated, the cost would tumble even further. On-site power generation, with use of CO_2 in stack gases could put the operating costs at about the level as conventional lime-alum systems. "Of course, if we add the costs of sludge handling, treatment costs are already in the same range," Thompson says. HMM



Packaged course. *Professor and policymakers from developing countries discussing industrialization (r. to l.)—Arthur Stern (U.S.); Zenon Baginski (Poland); Avinoam Shenhar (Israel); Alice Attuah (Ghana); Walter Witt (Chile); and Moncef Ben Abdallah (Tunisia)*

Training developing countries' leaders

This month, officials of the Agency for International Development (AID) and the United Nations Industrial Development Organization (UNIDO) hosted a debriefing and evaluation session for 29 senior policymakers from 18 developing nations. These policymakers—representing nations which include Indonesia, the Philippines, Korea, Paraguay, Chile, Brazil, Ghana, Kenya, Tunisia, Israel, Poland, Romania, and Hungary—had just completed a demonstration training course on the environmental aspects of industrialization.

Developed and presented by the Department of Environmental Sciences and Engineering, University of North Carolina (Chapel Hill), the course represented a U.S. response to one of a series of recommendations emanating from last June's UN Conference on the Human Environment in Stockholm which stressed the need for new approaches to environmental training and, in particular, training relevant to the special problems of developing countries. Both the Environmental Protection Agency and the Council on Environmental Quality endorsed and supported the program.

The 10.5-week course, which formally got under way on January 22, focused on environmental problems associated with industrialization. The decision to focus on the industrial sector was made in recognition of the fact that the U.S. has extensive information and experience on both the identification of the environmental problems and, most important, on methods and technologies for actually solving the problems.

One of the major goals was to end up with a packaged training program on the environmental aspects of industrial development that could be presented by other institutions in both developed and developing countries. The course, funded through separate contracts with AID and UNIDO, had a total cost estimated close to $125,000, which covered international and domestic travel, field trips, course development and documentation, and honoraria for guest lecturers.

Training of 29 policy makers from 18 developing countries will meet pressing industrialization demands

The format of the course included a series of lectures and discussions at the university which dealt with a wide spectrum of the environmental aspects of industrialization—air pollution, water and waste water treatment, land use and population, industrial hygiene, and organizational requirements—and also extensive field trips to industrial facilities throughout the southeastern United States. In addition, a one-week in-depth study at the industry of each participant's choice was provided.

Industry helps

U.S. industry played a key role in the course. Each policymaker spent 2.5 weeks on field trips, visiting the facilities of some 30 participating companies which represented heavy, light, and mechanical and engineering industries. Then each of the foreign representatives spent an entire week at one of the plants for an in-depth study of environmental problems and possible remedial measures of special interest to his country. Cooperating "heavy industry" firms included International Paper Co., Wellman Power Gas, Inc., Lonestar Cement Co., Farmland Industries, Cosper Foundries, American Cast Iron Pipe Co., Humble Oil Co., and Kaiser Aluminum.

The "light industry" firms included Cone Mills Industries, Thomasville Furniture Industries, R. J. Reynolds Tobacco Co., Sanford Brick and Tile Co., Fieldale Corp., Robert and Company Associates (Architects & Engineers), and Coca-Cola, USA. The third group—the mechanical and electrical engineering industries—included Tennessee Valley Authority, Widow's Creek Thermal Power Plant (Chattanooga, Tenn.), Raccoon Mt. Thermo-Power Plant, Brown's Ferry Nuclear Power Plant, and the National Fertilizer Development Center.

In addition, industrial officials, as well as personnel of the U.S. Environmental Protection Agency and their counterparts from a number of state environmental control organizations, presented lectures during the classroom phase of the course.

At the end of the training course the policymakers were taken to Washington, D.C., for debriefing, evaluation, and presentation of "diplomas." It is anticipated that this packaged program will lead to, among other ideas, regional seminars in developing countries, possibly organized by the participants in this first-of-its-kind course. Now, the participants are headed for home; hopefully each will play a major role in strengthening his country's environmental awareness and capabilities in the years ahead. SSM

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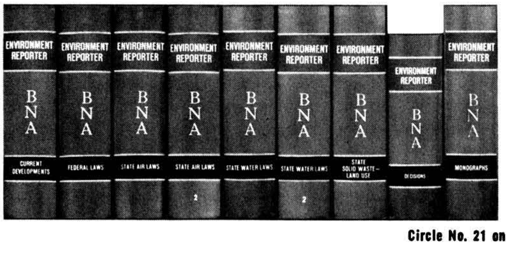

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FEATURE

Solid waste disposal: incineration or pyrolysis

James A. Fife
Metcalf & Eddy, Inc., Boston, Mass. 02116

Combustion processes not only reduce volume and weight of municipal refuse but also could produce steam or electricity

For centuries, man has, and still is, in many cases, disposing of solid wastes without preprocessing to reduce volume and/or weight. With widespread prohibition of open burning, many communities now realize that this practice may not be continued without inordinate consumption of land areas designated for waste disposal purposes. Not only are these areas hard to find at reasonable distances from refuse sources, but designation of a site for disposal usage is politically difficult, and the acquisition of the necessary approvals is almost impossible in many cases.

Several systems are available for consideration when the land-use rate of a disposal site must be reduced. Some of these reduce volume only, such as shredding followed by on-site, in-place compaction or high density compaction (or baling) followed by direct placement in the landfill. Combustion processes, on the other hand, reduce not only the volume of the refuse, but also its weight. While weight reduction is of no consequence with respect to landfill area use rate, the factor of reduced weight may be most important when the waste must be transported over significant distances. Table I compares the waste weight reduction capabilities and resulting waste densities of disposal systems available today.

Further elements to consider in waste disposal include the "environmental-insult" potential of the material disposed of on land, costs of the proposed volume reduction system vs. tangible and intangible values of the land that will be saved, and the socio-political public acceptance potential of the proposed process. Incineration systems suffer particularly, at present, in the latter respect. Although salvage or recycling is not new and does not at this time represent a major capability to reduce the rate of flow of waste materials, it must be considered as a mechanism to reduce the land use rate.

Incineration

In defining "incineration," one infers a combustion process to reduce the weight and volume of a waste on a controlled basis. The term is not used with respect to burning any material other than waste, and differs specifically from the definition of the term "pyrolysis" in this respect.

Modern incinerators differ markedly from their forebears specifically with respect to their ability to operate in compliance with modern air pollution control regulations, and with respect to the amount of manual labor required for furnace charging, stoking, and residue removal. Older plants are usually the batch-fed type, in which each furnace charge is separately dropped onto the fire bed, and residue is removed from the furnace in an intermittent or cyclical basis. Older systems are equipped with stationary grates requiring hand-stoking of the fuel bed, while more recent batch-fed plants are equipped with mechanical stokers.

Modern furnaces are the continuous-fed, mechanically stoked type, and are so arranged that feed and residue-discharge openings are continuously sealed while process materials flow through the openings. The continuous-feed arrangement (Figure 1) improves combustion and the air pollution control performance.

Both of these systems are arranged for refuse burning on grates. Recently, several modern facilities have been built using suspension-burning principles which may be divided into two categories: those which suspend the burning fuel in the gas stream in the combustion enclosure, and those which suspend it both in the gas stream and in another medium, the fluidized bed. Although the principles are not new to the power or process industries fields, the application of suspension burning to refuse is innovative at this time. Advantages of flue gas stream suspension burning include an ability to respond more rapidly to automatic control, an initial cost saving due to the lack of grate surface and mechanical stoking devices, and an ability to achieve complete combustion with a much smaller percentage of excess air in the furnace (which represents a significant economy where the refuse is a useful fuel and each Btu has a value). Both suspension and fluidized bed firing require piece-size reduc-

TABLE I

Weight reduction and density of solid waste

						Sanitary landfill	
Process system	**Shredding**	**Baling**	**Conventional incin.**	**High-temp incin.**	**High-temp pyrolysis**	**With track dozer**	**With compactor**
Weight reduction, %	0	0	75	75	75	0	0
Density of processed waste (lb/yd^3) in final disposal site	1000	1600	1200	2750	2750	750	1200

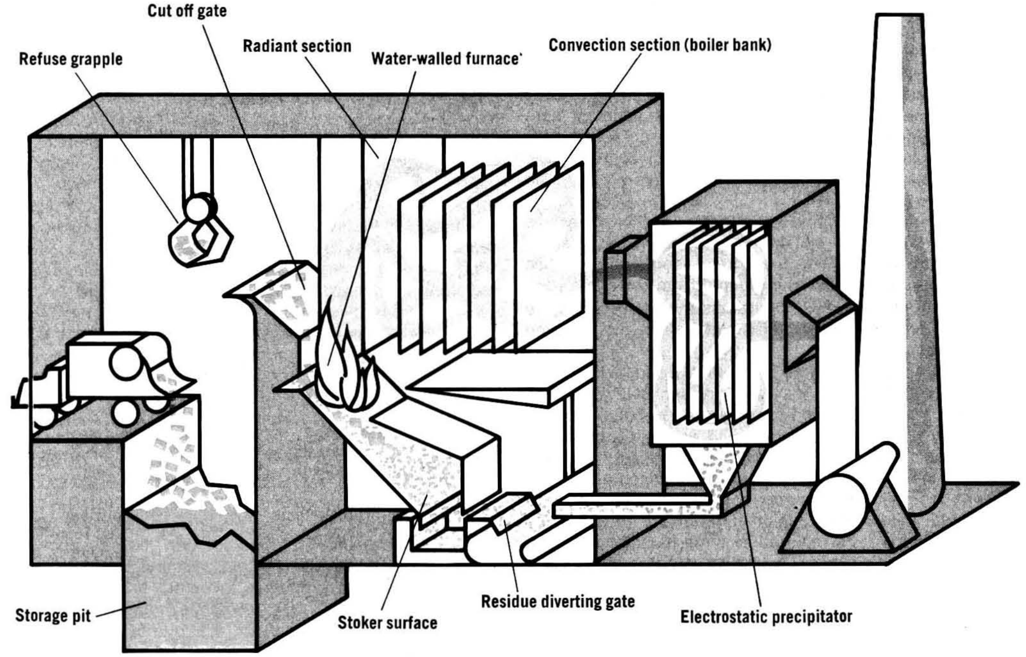


Figure 1. *In a continuous-feed, mechanically stoked incinerator, openings are sealed during process materials flow*

tion (or shredding) of the refuse mixture prior to feeding to the reactor—primarily to reduce the amount of residence time required in the combustion zone. Shredded material also has much improved handling characteristics, enabling conveyor-type feed systems and an inherently smoother furnace combustion process.

Fluidized-bed suspension burning systems have all of the advantages mentioned above, plus one which is important where a system must operate intermittently, for example, one shift per day. Fluidized beds, usually sand, comprise a "thermal flywheel" of large capacity. When the operating temperature is reached, they retain heat over a long time period, losing only about 200°F during an overnight shutdown. The savings on auxiliary fuel for preheat on the next start-up are appreciable and tend to offset fuel preparation costs. Fluidized beds are used routinely for many industrial applications and in sludge incineration systems at smaller sewage treatment plants.

Another new type of incinerator system is the slagging, or high-temperature, process. Originated in Germany and developed in the U.S. by American Thermogen, Inc. (Whitman, Mass.), these systems operate at about 3000°F, a temperature sufficiently high to melt, or slag, metals and ceramics. Residue discharged from the reactor is a viscous heavy fluid, or "melt," and can be either air-quenched or water-quenched. When water-quenched, the melt forms a granular, sandlike material known as frit, which appears to be alloyed metal surrounded by a ceramic, mainly glass. The residue, tested in Metcalf & Eddy's laboratory, is entirely inert, a property totally different from that exhibited by residue from a conventional or nonslagging furnace. American Thermogen's system requires firing auxiliary fuel to maintain the necessary elevated furnace temperature. Although the system was originally designed and a pilot plant built to fire coke in conjunction with refuse, control system response was too slow, and a second version of the pilot plant incorporates oil/gas dual-fuel burners at the base of the reactor, with reportedly much improved performance.

Smaller plants may now choose to use the "starved air," package-type furnaces made by several larger firms. With capacity up to 25 tons/24 hr, these batch-fed furnaces operate without underfire air systems to minimize entrainment of particulate matter from the fuel bed, and are afterburner-equipped for total burnout of volatile matter. These starved air units are, in a sense, pyrolysis systems rather than incinerators. Their air pollution control performance is excellent, and they can meet stringent codes without expensive flue gas-cleaning equipment. As might be expected, volume and weight reduction achieved is not so good as with more complex systems, and this batch feed arrangement involves hand removal of the residue. Charging systems include manual feed from containers, or the use of a small tractor moving material into a ram-equipped charging box. Investment costs are relatively low as compared with more complex systems, although operating costs may be increased due to the fuel requirements for the afterburner.

Wastes from incinerators

Incineration plants normally produce three waste streams with a potential to affect the environment: residue, a mixture of solids normally disposed to the land in sanitary landfills; flue gas, which is released to the atmosphere after treatment to remove particulate matter; and waste process waters, which are generally highly contaminated while in contact with residue or flue gas. Air and water pollution control codes are effective in regulating the qualities of these effluents, but solid residue is not, to the knowledge of the author, regulated.

Federal regulations ("Standards of Performance for New Stationary Sources") require that new incinerators be designed to emit flue gas with a particulate matter concentration not greater than 0.08 gr/scf corrected to 12% CO_2. Starved-air systems meet this requirement without gas-cleaning equipment, while conventional furnaces require wet scrubbers or electrostatic precipitators with 99% efficiency for compliance. Although costly, such efficient equipment is available with today's technology. Some states and larger cities have adopted more stringent codes—Maryland requiring 0.03 gr/scf at 12% CO_2, and Massachusetts with 0.05 gr/scf at 12% CO_2. These codes, in effect, prohibit incineration within the area of jurisdiction.

Since there is very little sulfur in refuse, SO_x emissions from incinerators are not of great concern. NO_x emissions do not occur at normal furnace temperatures when refuse is burned, but may be emitted from sewage sludge incineration systems. NO_x emissions may also become a problem with slagging systems with strict air pollution control codes.

Process water which has been used to quench residue is normally alkaline and may contain high BOD if the furnace is not being operated to produce a well-burned residue. Flue gas cooling or scrubbing water, on the other hand, is acidic, and normal treatment includes mixing the two streams for neutralization prior to discharge. Both streams contain high concentrations of dissolved and suspended solids, but additional treatment for dissolved solids removal will be required in some jurisdictions. Systems not including gas cooling or residue quenching, such as the starved-air and some fluidized-bed units, will not generate waste process waters requiring treatment.

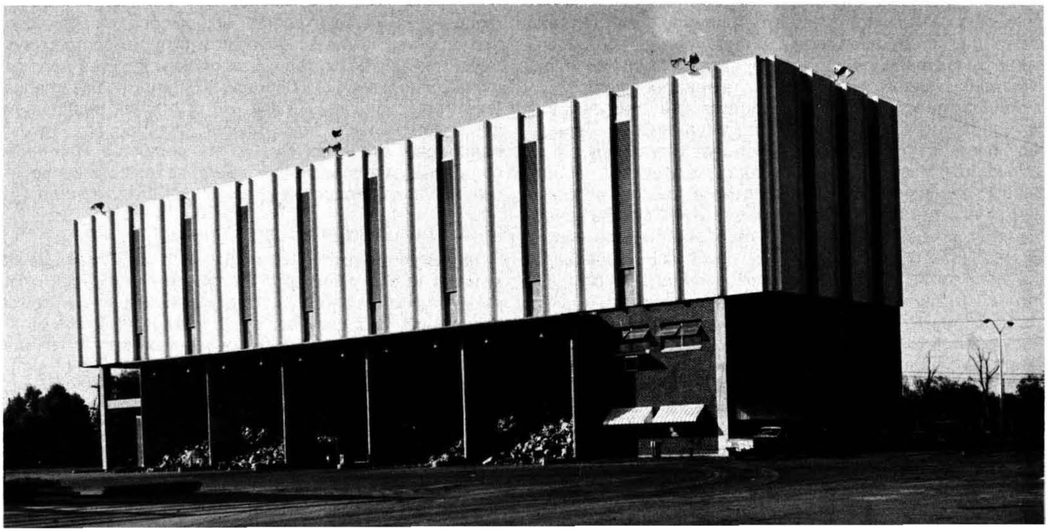
There are no well-established regulatory codes governing residue quality, and no standard test methods are known for incinerator residue in the U.S. at this time. Performance standards are usually included in specifications, however, and a typical requirement would allow no more than 4 or 5% (wt) unburned organic and a maximum or ½% (wt) putrescible material in the dry residue. These requirements are met by well-operated conventional systems; slagging systems, as previously indicated, would be expected to produce a totally sterile residue.

Heat recovery equipment may be incorporated into both conventional and slagging incinerator systems. Conventional systems may include this capability through a downstream waste heat boiler associated with a refractory furnace, or by building the furnace with water-cooled walls as a boiler. The boiler would normally also include a "convection section," or a "boiler bank," and either

System	**Boiler**	**Normal furnace temp**	**Lb steam/ lb refuse**
Conventional	Downstream waste heat	1800	1.0
Conventional	Water-walled furnace	1800	3.0
Slagging	Downstream waste heat	3000	3.3

System	**Manufacturer**	**Products**	**Status**
Conventional	Monsanto-Envirochem	Char, fuel gas, fuel oil	Pilot plant (St. Louis, Mo.)
Conventional	Garrett Div., Occidental Petroleum Corp.	Char, fuel gas, fuel oil	Pilot plant (San Diego, Calif.)
Slagging	Torrax Systems Inc.	Frit	Pilot plant (N. Tonawanda, N.Y.)
Slagging	Urban Research & Development Corp.	Frit	Pilot plant (E. Granby, Conn.)
Slagging	Linde Div., Union Carbide Corp.	Frit Uses pure O_2 instead of air for combustion (NO_x emission minimized)	Under design

Modern. *The East Side Incinerator in New Orleans, La., (below) has a capacity of 400 tons of municipal refuse per 24-hr day. Such new incinerators differ from older models in the ability to operate in compliance with air pollution control regulations and in the amount of manual labor for furnace stoking, charging, and residue removal*



type of unit would normally cool the flue gas from furnace temperature (1800°F) to 500° or 600°F. The slagging process is not compatible with water-cooled furnace construction, but such systems successfully have been equipped with downstream waste heat boilers. Steam production potentials for various incinerators, based on refuse with a higher heating value of 5000 Btu/lb, are shown in Table II.

Heat recovery from solid waste processing has two associated benefits beyond the potential value of the energy itself. First, the resulting gas cooling, without need for air dilution or evaporative cooling with water, produces a minimum volume of flue gas requiring treatment. Significant savings accrue owing to this minimum volume, particularly where high-efficiency scrubbers or precipitators are required. Furthermore, in areas where the regulatory code is in terms of allowable particulate matter concentration, the lower flue gas volume passing to the atmosphere also means a lower total weight of particulate matter emission. Secondly, when recovered heat is put to some beneficial use, a corresponding quantity of fossil fuel would not be burned, thus eliminating all emissions from this source. The heat recovery-thermal reduction method for solid waste processing has been widely used in Western Europe for many years.

Pyrolysis

Like incineration, pyrolysis is a controlled combustion process. Unlike the term "incineration," however, pyrolysis or destructive distillation does not imply that a waste is being burned; and in fact, the pyrolysis process has been used for years by industry—for example, production of charcoal and methanol from wood, and coal gasification. The process requires raising the fuel to a temperature at which the volatile matter will distill (boil off), leaving carbon and inert material behind. The carbon and volatiles do not burn in the process owing to an intentional deficiency of air in the primary reactor. Volatile matter may be burned off as waste in a secondary chamber to which air is added, or the off-gas may be cooled and condensed to selectively recover oils and tars. Alternatively, the gases may be cleaned and used as a gaseous fuel.

Volume and weight reduction of wastes is accomplished by the pyrolysis process, although obviously conventional pyrolysis does not accomplish these to the same degree as does incineration. High-temperature, or slagging, pyrolysis does produce results equal to those obtained from slagging incineration and may in the future accomplish this without use of auxiliary fuel. This would be done by recycling the volatiles and burning them in the primary chamber to obviate the extra costs of the additional heat source required in slagging incineration.

Several different pyrolysis systems have been developed over the past few years for application to the solid wastes problem (Table III).

Table III points out that the application of pyrolysis to solid wastes processing is relatively new, and, in fact, no full-scale systems applied to municipal operations are operating in the U.S. at this time. Monsanto (St. Louis, Mo.) has sold a system with federal grant support to Baltimore, Md., and Torrax (N. Tonawanda, N.Y.) is currently negotiating a large contract with the City of New York. All development is by private industry, and those systems ready for marketing are offered on a proprietary basis in which design, construction, and usually operation are offered on a turnkey basis. Competitive bidding prior to purchase is possible, but bids are difficult to evaluate due to basic dissimilarities between the individual systems. All basically differ as to design and performance potential, and competing designs which would offer identical results are not available through the usual "consultant for design" and "contractor for construction" process. This statement is not meant to disparage, for the pyrolysis process holds real interest. It is meant, however, to indicate that comparison between pyrolysis and incineration systems is most difficult. Cost data from full-scale operating systems are not yet available, and there is no basis on which to assess the reliability of these new plants.

As with incinerators, pyrolysis plants may create emis-

TABLE IV

Incineration/pyrolysis systems evaluation

	INCINERATION		PYROLYSIS	
System feature	**Conventional**	**Slagging**	**Conventional**	**Slagging**
Residue density, lb/yd^3	1200	2750	Metals, ceramics, and charcoal	2750
Residue marketability	Low	High	Medium	High
Availability of manufacturers for competitive bidding	Many	Two American Thermogen, Inc. Dravo Corp.	Two Monsanto Enviro-Chem "Landgard" Garrett Research Division, Occidental Petroleum Corp.	Two Torrax Systems, Inc. Urban Research & Development Corp.
Reliability experience	80%	None	None	None
Bidding experience for cost data	Widely available	Some American Thermogen, City of Walden, Mass., negotiated contract	Some Monsanto "Landgard", City of Baltimore, Md., negotiated contract	None
Marketable process outputs	Heat, metals from residue	Heat, frit	Oils, tars, charcoal, heat, fuel gas	Oils, tars, frit, heat, fuel gas
Estimated owning and operating costs ($/ton), 20-year av[a]	6.55	8.30	7.00	8.95

[a] Based on ENR 1750, plant capacity 2000 tons/day, credit taken for sale of heat only at $0.60/10 million Btu.

Examples of manufacturers of pyrolysis or incineration equipment

Field-erected complete systems	Components for field-erected systems	Packaged units or small field erected systems
INCINERATION		
Combustion Engineering Inc. Dorr-Oliver, Inc. Envirotech Corp. Morse Boulger, Inc. MSI Industries, Inc. Nichols Engineering & Research Corp. Pyro Industries, Inc. Thermal Research & Engineering Corp. Zimpro, Inc. John Zink Co. Zurn Industries, Inc.	Bartlett-Snow Beaumont Birch Co. Bigelow-Liptak Corp. Coen Co. M. H. Detrick Co. Detroit Stoker Co. Dorr-Oliver, Inc. Envirotech Corp. Klenz-Aire, Inc. Maxon Corp. Morse Boulger, Inc. MSI Industries, Inc. Nichols Engineering & Research Corp. Pyro Industries, Inc. Thermal Engineering & Research Corp. Zimpro, Inc. John Zink Co. Zurn Industries, Inc.	Brule Incinerator Corp. C-E Air Preheater CE-Raymond/Bartlett-Snow Joseph Goder, Inc. Midland Ross Corp., Surface Combustion Div. Sanitas Technology & Development Corp. Zurn Industries, Inc.
PYROLYSIS		
Monsanto Enviro-Chem Systems, Inc. Union Carbide Corp., Linde Div.		C-E Air Preheater Midland Ross Corp., Surface Combustion Div. Prenco Mfg.

Note: List not exhaustive

sions to land, air, and water. By contrast, however, solid residues from nonslagging processes may be marketed as charcoal or as a filter-absorbent for use in waste water treatment. Since the process involves combustion in an air-deficient atmosphere, or with pure O_2, the volume of off-gas is lower than with incineration—a large benefit for air pollution control. The combustible gas would seldom be emitted, however, and would, more than likely, be burned as a fuel or processed for recovery of hydrocarbons. Torrax (Mark I), for instance, burns the gas in a secondary chamber and recovers the energy in a downstream waste heat boiler. Torrax (Mark II) is expected to recycle the gas to the primary reactor for burning there, thus eliminating the present need to burn fossil fuel to reach slagging temperatures. As with slagging incineration systems, frit from slagging pyrolysis units appears to have a high recycling potential for insulation materials, metal products, and for building materials. Pyrolysis can also be used in recycling cans to remove labels without oxidizing the base metal. (The system would be conventional, or nonslagging, in this case.)

Selecting the system

Incineration is a long-established process with well-known cost and reliability characteristics. Theoretically, it is highly capable of obtaining its intended results but suffers in reputation owing to low stringency of previous air pollution regulatory codes and the inattention of owners to proper operation and maintenance. Conversely, pyrolysis has not yet been applied in a real sense. When a new plant is proposed for solid waste disposal, experience shows that an incineration plant has almost no public acceptance potential, while the chances of public acceptance for a pyrolysis plant are excellent.

Where volume and weight reduction are the objectives, both processes can be considered. Both are compatible with "front-end" constituent segregation for recycling, and both produce solid residues which can be beneficiated for constituent reuse. Both have a potential for the recovery of heat energy at comparable rates and costs. Table IV lists the considerations involved in decision-making, and may be helpful where a choice is to be made.

Making the choice, then, is complex, and will involve the public acceptance potential, land value, and the largely unknown future availability and magnitude of long-term markets for some potential process outputs. Real cost data can be obtained only by actual competitive bidding, or from final negotiated contracts, and these data are not widely available for the new systems. Available information, however, indicates that the developers of the new systems are willing to proceed at costs which are initially competitive with conventional incineration. An early step, then, in making the decision, would be to obtain costs for system alternatives that are firm for the intended application, and which reflect the degree of design, construction, and operating services to be furnished by prospective suppliers. Documents used as a basis for bidding or negotiating must be comprehensive and should be prepared in such a way that the data received in response are truly comparable.

Evaluation of competing proposals is impossible unless all are on the same basis as to system capacity, anticipated throughput, required reliability, and uniform price data for the sale of system-produced energy or by-products. All must be designed for the same standard of code compliance, each with the same provisions for future increased regulatory stringency. Although pyrolysis systems offer a greater range of potentially marketable by-products, the true value of these by-products will vary with their location and distance from the market. Therefore, a universally applicable conclusion cannot be drawn, and each case must be evaluated in its own context. Also, decisions must no longer be based on technical considerations alone. Socio-political considerations may easily outweigh the decision which would be made by a typically conservative engineer, especially when his public works experience has long been based on principles requiring maximum security for invested public funds.

James A. Fife *is a vice-president and staff consultant for Metcalf & Eddy, Inc., consulting engineers. Mr. Fife is a specialist in the field of refuse collection and disposal and also in the air pollution control field. He is a consultant to the office staff regarding incineration, sanitary landfill, and other processes for refuse disposal, and concerning refuse collection system organization and economics.*

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Office of Saline Water
Washington, D.C. 20240

Progressively stricter effluent discharge standards (best available technology by 1983 and "zero" discharge by 1985) lend added impetus to water recycling. In certain areas of the U.S., notably southern California, the pressure of increasing urban growth has seriously taxed the supply of fresh water. As a consequence, adoption of "open-leg" municipal reuse techniques is imminent. In this approach, applications involving aquifier recharge, surface reservoirs, and/or irrigation are interposed between the point of discharge and the user.

A number of dissolved organic and salt contaminants are introduced during many of the industrial and municipal water-use cycles. Control of dissolved material is a necessary step in most reuse schemes; thus, desalting technology has an important and major role to play in water reuse and pollution abatement.

The Office of Saline Water (OSW), U.S. Department of the Interior, has led Federal Government efforts in desalting, having spent approximately $250 million sponsoring industrial, university, and state efforts in desalting. OSW develops promising desalting processes to the point where the technology appears commercially viable. Until recently, OSW's effort has been confined to desalination of seawater and brackish water as a source of supply for municipal and industrial usage. A varied inventory of desalting equipment exists as a result of significant efforts on the part of OSW and private industry. The fact that this equipment, with suitable modification, can be applied to water reuse applications is largely fortuitous. The maturation of desalting technology coincides with current ecological concern.

While desalting is generally a secondary objective of the reuse cycle, it is, in many instances, an essential one. Reuse water usually has low levels of salinity (500–1500 ppm total dissolved solids); as a consequence, the overall salt rejection efficiencies may be compromised below those values normally associated with the conversion of brackish water. This is not to say that high selectivities for specific contaminants, for example, trace heavy metals, toxic elements, and pesticides, should not be preserved, and indeed encouraged. In some cases, especially where potable water is to be produced, supplemental posttreatments are required to remove or render inactive certain noxious contaminants and viruses which may skirt the desalination process.

Much of the commercially available water reuse–desalting hardware represents first-generation equipment. This equipment, particularly in the reverse osmosis (RO) -ultrafiltration (UF) field, has evolved from the application of a new unit operation to a number of specialized, small-scale (less than 1 mgd) applications. In most instances the economy of scale-up, for example, the deployment of large-capacity items of equipment, has not been fully realized (Figure 1).

Industrial water reuse applications covered in this article have initially evolved, with few exceptions, from meeting waste water discharge standards rather than economic considerations. For relatively small volumes of waste which contain a recoverable by-product that may underwrite a portion of treatment costs, overall costs of 40–60¢/1000 gal are tolerable. This is not the situation for major pollution abatement applications, involving petroleum complexes, chemical plants, and municipal water supplies where the cost for reuse-desalting must compare favorably with the conventional process train of acquisition, conditioning, and waste treatment. As waste treatment processes become more elaborate to meet higher quality discharge standards, treatment costs will escalate to the point that state-of-the-art reuse-desalting becomes a tenable alternative. Obviously, the state-of-the-art reuse-desalting processes are adopted out of the necessity of timely compliance to pollution control legislation.

Reuse-desalting costs can be expected to improve as the benefits associated with scale-up, large-capacity

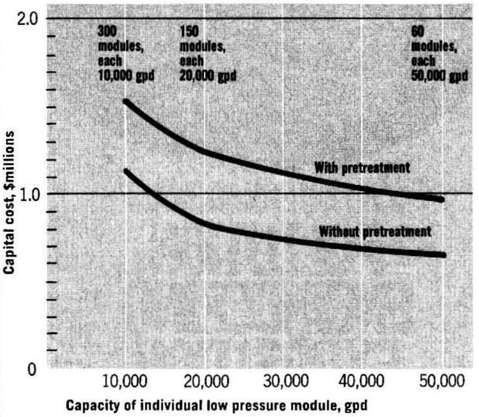


FIGURE 1.

Plant cost vs size of RO modules

3.0 mgd reverse osmosis plant

TABLE I

Summary of reuse-desalting commercial endeavors

Company	Equipment description/configuration	AREA OF PROBABLE APPLICABILITY								
		Commercially viable at present			Future					
		a	b	c	d	e	f	g	h	i
Abcor Cambridge, Mass.	UF/RO tubular	X	X						X	X
Westinghouse Philadelphia, Pa.	UF/RO tubular	X	X						X	X
Philco Ford Newport Beach, Calif.	UF/RO tubular	X	X						X	X
Dorr-Oliver Stamford, Conn.	UF flat-plate thin film	X	X						X	X
Romicon Woburn, Mass.	UF annular thin channel	X	X						X	X
GESCO San Diego, Calif.	RO sprial wound				X	X	X	X		X
Rex Chainbelt Milwaukee, Wis.	RO Du Pont hollow fine fiber				X	X	X	X		X
Permutit Paramus, N.J.	RO Du Pont hollow fine fiber				X	X	X	X		
Envirogenics El Monte, Calif.	RO tubular and spiral wound	X	X		X	X	X	X	X	X
Dow[a] Midland, Mich.	RO hollow fine fiber UF hollow fiber dialyzer (specialty)				X	X	X	X		
Monsanto[a] Durham, N.C.	RO hollow fiber				X	X	X	X		
Ionics Watertown, Mass.	Modified ED unit			X						
Aquachem Waukesha, Wis.	Multistage evaporation				X			X	X	
Resource Construction Seattle, Wash.	Vapor recompression distillation				X			X	X	
Colt Industries Beloit, Wis.	Vacuum freezing-vapor compression				X			X	X	
Avco[a] Wilmington, Mass.	Secondary refrigerant freezing				X			X	X	

[a] Hardware currently under development, not commercial.

modules, and improved equipment and systems make their mark on the cost effectiveness of the reuse-recycle process leg. Much of OSW's effort in the development of large-scale brackish water conversion systems (Figures 2 and 3) is directly applicable to effecting similar improvements in reuse-desalting hardware. Thus, it is anticipated that rapid strides can be made in improving the status of reuse-desalting into a competitively viable unit operation. With the total assimilation of advanced desalting technology into the reuse-desalting process, treatment costs of 30–40¢/1000 gal (desalting is 15–20¢) appear to be a realistic target.

Developing reuse-desalting applications

Three "reuse-desalting" applications have developed on their commercial merits, namely, • the reuse of electropainting rinses (*a*); • the fractionation and ultrafiltration of cheese whey (*b*); and • the point-of-source manufacture of sodium hypochlorite as a waste treatment biocide (*c*). A number of feasible, specialty applications, which have resulted from pollution control considerations, are under development. These include but are not limited to • cooling tower and boiler blowdowns (*d*); • petroleum stripping waters (*e*); • plating rinses (*f*); • metal finishing rinses (*g*); • pulp and paper spent liquors (*h*); and • municipal sewage effluents (*i*).

In primary reuse-desalting processes, a concentrated brine stream which requires further processing is produced. Environmental considerations dictate that this stream be concentrated until dry, containable, and, it is hoped, until usable solids are produced. Depending on the content and size of the brine stream and location of the plant, a number of desalting processes are used to achieve final concentration: electrodialysis (ED), vapor recompression evaporation, multieffect evaporation, freezing, and ponding, etc. The contribution of these and similar processes to the total reuse-desalting system should not be overlooked. A summary of a selected group of manufacturers who have capabilities in the area of reuse-desalting is shown in Table I. The reuse-desalting applications are presented in order of anticipated development; paradoxically, the more difficult, large-volume applications in terms of augmenting water supply are ranked last.

Electropainting rinses

Electropainting is widely used by manufacturing industries (automobile, truck, for instance), which require a uniform primer coat on an intricate assembly. The paint is applied by dipping the electrically charged part into a dip tank containing an emulsion of resin and pigment particles. The electrostatic charge causes the paint colloid to migrate to the surface of the part and to coalesce into a uniform film. When the object is lifted from the

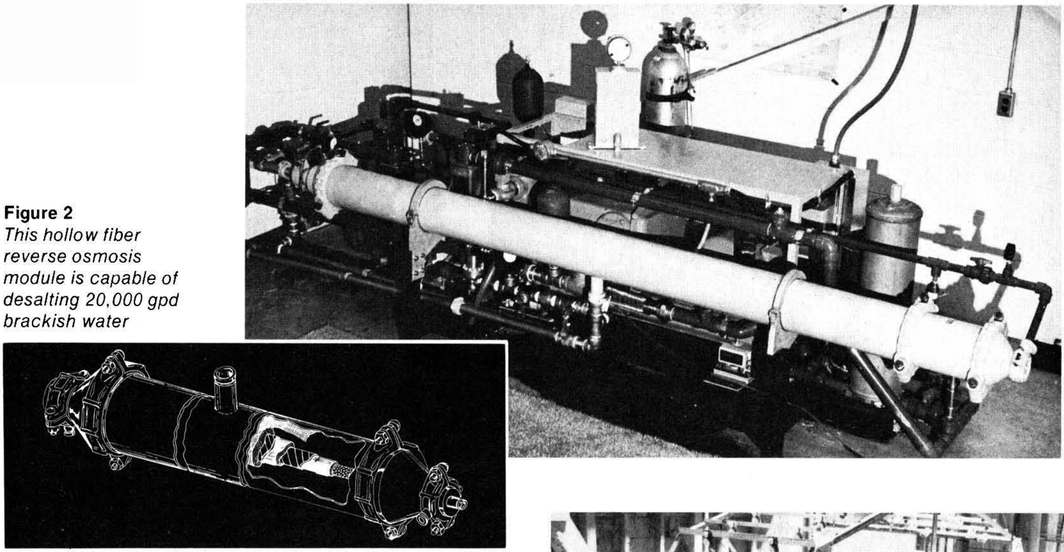


Figure 2
This hollow fiber reverse osmosis module is capable of desalting 20,000 gpd brackish water

painting bath, excess paint (dragout) is removed by rinsing, and the rinse water is returned to the dip tank. The return of the rinse, coupled with paint usage, lowers the concentration of paint in the dip tank. Since a constant, optimum concentration of paint is required to maintain proper quality control, water must be continuously removed from the dip tank. In addition, certain ionic substances—chromates, phosphates, chlorates, and sulfates—are picked up during surface pretreatment operations and progressively contaminate the dip tank. Make-up paint, with surfactants (amines or hydroxides) to stabilize the paint emulsion, is added to the dip tank to maintain the paint inventory.

Removing excess water and contaminants from the dip tank may be accomplished through ultrafiltration of a side stream from the dip tank (Figure 4). The ultrafiltration unit generally consists of a tubular membrane assembly in which the paint emulsion is circulated inside the membrane tubes at 15-50 psi pressure. Rapid, highly turbulent cross flow (10–20 ft/sec) is maintained past the membrane surface to retain the paint particles in the turbulent core and prevent blockage due to the accumulation of paint on the membrane surface. The paint solids are returned to the dip tank for reuse while the excess water containing trace salts and stabilizer is used as a rinse and/or is discarded.

Broad industrial acceptance of this process has resulted from cost savings effected by a drastic reduction of paint dragout losses. Payout time for ultrafiltration equipment to realize these savings is generally four to six months.

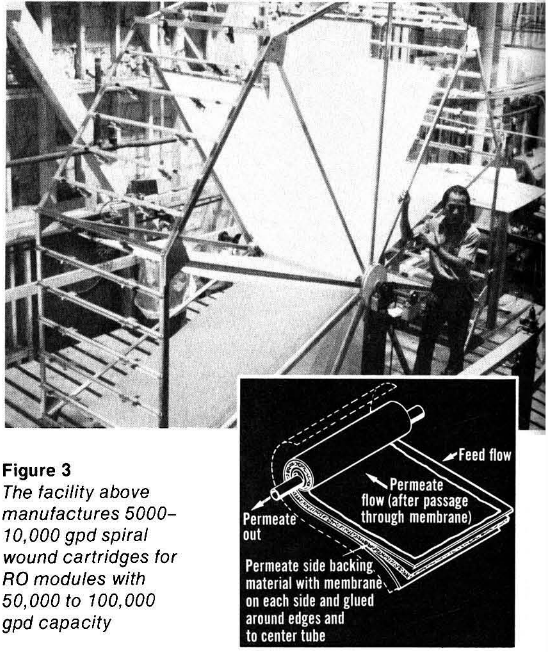


Figure 3
The facility above manufactures 5000–10,000 gpd spiral wound cartridges for RO modules with 50,000 to 100,000 gpd capacity

Fractionation of cheese whey

Cheese whey is normally discarded to sewage systems and waterways. Due to its mainly lactose sugar content (5 wt % for cottage cheese whey), it possesses a high biological oxygen demand. Whey also contains appreciable amounts of protein as casein (0.8 wt.% for cottage cheese whey). By employing a two-step ultrafiltration/reverse osmosis process (ES&T, May 1971, p 396) for fractionating cottage cheese whey into valuable protein and lactose concentrates for food products, cleanup costs of the whey wastes may be recouped by the sale of the by-products.

The ultrafiltration/reverse osmosis (UF/RO) plant must conform to normal dairy processing practice. Tubular membrane modules are housed in cabinets where "cleaning in place" sanitizing solutions are sprayed to the outside of the tubes while also being pumped through the interior of the tubes.

A representative UF/RO system consists of a series of UF modules for treating the raw whey from a temperature-controlled feed tank. The UF system separates the larger protein molecules from the smaller sugar molecules which, along with salts, pass through the UF membrane. The protein is retained in the concentrate recirculated to the feed tank to achieve concentrates of 10–12 wt % solids in the final concentrate. The solids contain approximately a 6 to 4 split of casein to lactose. The UF concentrate is then evaporated (scraped surface or falling film evaporation) to provide the 40–50 wt % solids required for the final spray-drying operation. The lactose containing permeate from the UF section is cooled and collected in an interstage tank. It is then pressurized and pumped in a once-through mode through a tapered RO section, thereby effecting a fourfold increase in lactose concentration (6–25 wt %). At higher concentration factors, lactose begins to precipitate from solution and may scale the membrane. The lactose concentrate is fed to a conventional crystallization train consisting of such items as a scraped surface evaporator, crystallizers, centrifuges, dryers, and baggers.

Preliminary conclusions indicate that the total by-product protein and crude lactose produced will significantly offset processing and pollution abatement costs.

On-site generation of hypochlorite

The use of oxidizing biocides, such as sodium hypochlorite, to control the biological activity of waste water is increasing. On-site generation of sodium hypochlorite is an attractive alternate to tank trucking and maintaining an inventory of reagents. Sodium hypochlorite is generated by an electrolytic membrane cell producing chlorine gas and sodium hydroxide solution which are subsequently reacted outside the cell to produce 5–10% sodium hypochlorite solution. Production and use of hypochlorite are less hazardous than direct injection of chlorine gas which is highly toxic and corrosive. Improvements in safety, reliability, and economy result from using a hydraulically impermeable cation exchange membrane.

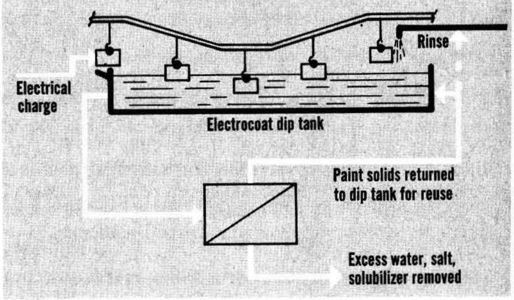
The hypochlorite generator is composed of a series of back-to-back membrane cells mounted in a "plate and frame" type of device. The membrane cells consist of an anode (a titanium screen coated with a special metal oxide coating), an anode compartment spacer, a perfluorosulfonic acid cation exchange membrane, a cathode compartment spacer, and a cathode (expanded mild steel). Filtered, fresh water is purged through the cathode compartments, while a sodium chlorine brine solution is passed through the anode compartments. The chlorine gas and spent brine anolyte is sent to a trapped disengagement section. The chlorine gas flows overhead to a reactor where it reacts with the caustic formed in the cathode compartments to produce the hypochlorite. The hydrogen gas from the cathode compartments is diluted with air well below explosive limits and vented off to the atmosphere. Costs for this system are approximately two thirds of those associated with the purchase and delivery of sodium hypochloride to the treatment site.

Blowdowns

Environmental discharge standards require control and reduction of dissolved solids such as sulfates and radioisotopes, such as from nuclear plants, contained in process blowdown streams. Blowdown waters originating from cooling towers and both conventional and nuclear boilers are amenable to established brackish water desalting processes. The low salinity levels generally involved, 500 to several thousand TDS (parts total dissolved solids), encourage membrane-based processes, low-pressure reverse osmosis, and electrodialysis for the initial concentration step in desalting.

However, chromate-base corrosion inhibitors are poorly rejected by some RO membranes when used with cooling tower waters. Thus the desalted permeate, if recycled to the cooling tower system, would significantly reduce the net consumption of this inhibitor.

FIGURE 4.
Using UF for electropainting baths



With conventional boiler blowdown, in addition to the normal dissolved ion content, the membrane system must remove phosphates and amines (chemical treatment agents for the maintenance of pH to suppress corrosion). In nuclear applications, borate leakage and/or carry-over from neutron absorption systems pose a potential problem since borate rejection is normally poor. However, under alkaline conditions (pH of 10.0–11.0), polyamide base membranes may adequately reject the borates.

Approximately 150 billion gal per year of cooling tower wastes are generated by industry and the utilities (3–1 ratio between manufacturing and power generation). Cooling towers, more than likely, will be used more and more within the power industry to meet thermal discharge standards. About 10 billion gal of boiler blowdown are produced annually.

Petroleum stripping waters

About 10% of the waste water attributed to refinery operations represents waters which contain extracted ammonia, hydrogen sulfide, and phenols along with trace organics from various petroleum fractions. The presence of these compounds preclude direct discharge into a waterway. Ammonia and hydrogen sulfide are conventionally removed by steam stripping. The bulk of the phenols and organics are biologically oxidized, with considerable difficulty, prior to discharge. However, reverse osmosis coupled with appropriate chemical pretreatment and post-treatment oxidation can supplant the sometimes unreliable physicochemical-biological step. Development of improved physicochemical waste treatment processes for petroleum stripping waters appears to be a certainty.

Plating rinses

In the plating process only a small fraction of the metal inventory—nickel, chromium, for instance—present in the plating bath is actually deposited. A large majority of these often expensive materials are chemically precipitated, discarded, and eventually lost to the environment. Membrane processes can purify low-level plating rinse wastes to concentrate the plating ions to levels where recycle to the plating bath is economically attractive.

Metal-finishing rinses

In metal-finishing operations large quantities of water are used for cooling and lubrication. The water usually picks up trace quantities of heavy metals and organics during use. Generally this water is discharged to a receptor upon cooling, but strict pollution discharge standards relating to the toxicity of heavy metals are stopping this practice.

This situation is similar to the case of plating rinses—physicochemical processes must be utilized to obtain an acceptable effluent. Two alternatives exist: to use a desalting process, for example RO or ED which would produce a water suitable for reuse and reduce water consumption; or to use a selective exchange process, for example, ion exchange (to displace heavy metals with an acceptable ion such as sodium without a reduction in water requirements).

Pulp and paper

The pulp and paper industry is a major water user. A wide variety of effluents results from the basic pulping processes and their numerous process streams. Strong cooking liquors (10–15% solids) are generally concentrated by multieffect evaporation and recycled within the mill or marketed. In some instances, such as for acid sulfite pulping, the volatile acids (SO_2, acetic, and formic acids) are combined with the condensate and comprise a major BOD source in the waste streams. Bleach plant effluents, originating from alkaline sulfate pulping, pose a difficult problem since they contain biological oxidation-resistant dissolved organics and salts (NaCl, Na_2SO_4). Complete control of such waste discharges by evaporation is expensive ($1.50–2.00/1000 gal). UF/RO used as a first step in the concentrator train is an attractive alternate.

Considerable research has been performed in this area. However, the research for promising results over a reasonable service life (1 year) has been hampered by: • high back-osmotic pressures associated with many of the waste liquors which require processing pressures of 600–800 psi; • high fouling tendencies possessed by these liquors which may result from the complexing of lignin sulfonic acids with polyvalent cations at the membrane wall; and • development of reliable tubular RO hardware which must endure severe operating conditions.

Progress is being made—dynamically formed lignosulfonate membranes formed on UF supports, in lieu of integral cellulose acetate membranes, have the potential to stop the leakage and failures associated with the harsh membrane cleaning cycles normally used with high fouling feeds.

Municipal sewage effluents

Wide-scale practice of municipal water reuse depends on need, costs, and public acceptance. A number of communities across the U.S. could improve the quality of their water supply by adopting reuse-desalting techniques. In several instances, a reuse-desalting system is superior to expanding the water supply via "straight" desalination of a brackish water source.

Southern California is an area where municipal water supply limitations appear to be limiting growth and economic development. The critical situation in the area has encouraged a number of water agencies to consider seriously development of alternate water supplies, including reuse. Ground water supplies in this region are being severely taxed and becoming subject to seawater intrusion. Sewage plant effluents, in conjunction with desalting techniques, are scheduled for reuse in charging and maintaining ground water aquifers. One advantage that reuse-desalting via aquifer recharge has for municipal applications is that while it "closes the loop," it does so in a manner psychologically acceptable to the general public. Several sewage reuse-desalting schemes are under consideration, including direct recycle:

Location	Process
Orange County, Calif.	Sewage effluent aquifer recharge diluted with desalted seawater
Escondito, Calif.	Desalt sewage effluent prior to aquifer recharge
Oceanside, Calif.	Sewage effluent recharge, desalt on withdrawal from aquifer
Ventura, Calif.	Desalt sewage effluent, sorb and oxidize organics, and recycle

Conventional biological treatment is an integral part of each of these candidate reuse systems.

A possible variation for municipal recycle is to utilize UF to remove suspended organics and clarify the water for recharge to an aquifer and to use RO as a complementary step to demineralize and purify the water when taken from the aquifer. A secondary posttreatment chlorination of product water should, of course, be performed as a precautionary measure.

Many of the waste treatment physical-chemical unit operations costs (flocculation, sedimentation, clarification, or absorption) are volumetric throughput controlled. By increasing the concentration and reducing the size of the process stream early in the process, proportionately smaller capital equipment costs and operating expenses are incurred. In many instances the efficiency of the process is improved; higher clarity supernates, more effective biological digestion, and direct oxidation, to name a few, are some of the anticipated outgrowths dealing with higher concentrations of contaminants.

One potential application concerns dewatering and disposing of sewage sludge which accounts for approximately 30% of sewage treatment costs. Sewage sludge is highly voluminous and generally 94% water. Pressure cooking of sludge (Porteous Process) greatly enhances the dewaterability—the sludge is only 50–60% water, and sludge volumes are reduced nearly an order of magnitude. However, the resultant supernate is heavily loaded with dissolved organics, and if recycled to a conventional treatment plant, an appreciable increase in biological loading occurs. RO and UF provide an attractive alternate to biologically processing the organically charged supernate.

The cost effective utilization of desalting processes in reuse applications can be achieved by optimizing the total system rather than simply suboptimizing the desalting process per se. Important progress has been made in desalting feeds that possess a high fouling potential: Recently, UF-dialysis has been used to remove side product salts from high-molecular-weight polymer suspensoids. The desalting process, such as RO or UF, may be used to create concentrated waste or process streams which may be dealt with in a more intensive fashion than the highly dilute waste or process streams normally encountered. The ability to produce and subsequently treat grossly concentrated waste streams, opposed to the treatment of dilute feeds, opens new and exciting possibilities in the area of industrial and municipal waste processing.

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Chemical Equilibrium Models of Lake Keystone, Okla.

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■ Several heterogeneous chemical equilibrium models have been developed which depict the concentrations of all principal inorganic chemical species in Lake Keystone, Okla. The models were based on the thermodynamic equilibrium condition of evaporite minerals (halite, gypsum, dolomite, calcite, and $SrSO_4$), clays (kaolinite, sodium montmorillonite, and calcium montmorillonite), and the liquid and gas phases which comprise the Lake Keystone drainage basin. Ten components were calculated by Gibbs phase rule, using analytical data for the total chemical compositions and the available thermochemical data. The model which simulated the experimental data most closely was based on the hypothesis that waters, originally in equilibrium with the common evaporite minerals of the Permian formation within the Arkansas River drainage basin, were diluted by fresher waters not exposed to these minerals as they flowed toward the reservoir. The waters then approached a state of chemical equilibrium with clay minerals which adjusted their final composition.

Chemical equilibrium models of natural water systems have been very useful in the past as a means to provide valuable insight into the processes that control the chemical composition of these systems (Garrels and Thompson, 1962; Kramer, 1965; Morgan, 1967). For example, comparisons of the models with real systems have helped isolate some of the principal regulatory processes, emphasized where further studies are needed, and abstracted simplified situations from the complexity of nature that could be understood and manipulated (Sillen, 1961, 1967; Stumm, 1964).

In this study, a series of chemical equilibrium models of Lake Keystone, Okla., are formulated and these are compared with chemical and physical observations made from May 1966 to June 1968. This appears to be a unique application of equilibrium models in that the reservoir receives waters drained from semiarid plains containing numerous sources of inorganic salts. These waters vary widely in both quality and quantity, and their impoundment results in many unusual chemical, physical, and biological interactions not commonly observed (Eley et al., 1967).

Lake Keystone is a riverine reservoir located on the Arkansas River in north central Oklahoma with the dam 15 miles upstream from Tulsa (Figure 1). The two chief tributaries of the reservoir are the Arkansas and Cimarron Rivers which converge about two miles above the dam to form the two main arms of the reservoir. The total drainage area of 74,500 sq miles extends from the Rocky Mountains in Colorado and New Mexico, across southern Kansas and northern Oklahoma.

The average rainfall in the drainage area varies from less than 16 in. in the western part to more than 30 in. in the east and there are notable seasonal annual variations. Spring is the wettest season with an abundance of rain from local heavy showers and thunderstorms. Summers are generally dry and drought conditions are not uncommon. In the fall, the rains are generally more steady. The average volume of water flowing past Tulsa is about 4.5 million acre-ft per year.

In northwest Oklahoma and central Kansas, rocks of the Permian formation outcrop (Jordan, 1967). These rocks are composed largely of the evaporites: gypsum, halite, and dolomite. Gypsum frequently occurs at the surface or at shallow depths beneath shales. Halite occurs at shallow depths below the surface as isolated crystals, in discontinuous shaley lenses, and in thin layers.

Gypsum is relatively soluble and readily available to surface and ground waters. Under favorable geological conditions, fresh water circulates downward through the salt-bearing beds and dissolves large quantities of halite as well as gypsum. Numerous salt water springs, salt plains, salt water seeps, and salt marshes, containing as much as 200,000 parts per million chloride, occur in these areas (Ward, 1961; Ward and Leonard, 1961).

Experimental Procedures

Samples were taken directly behind the dam at depths of 1–4 meters apart from the surface to the reservoir bottom (22 meters). The properties included in the total water analysis were temperature, dissolved oxygen, dissolved CO_2, suspended solids, dissolved solids, pH, and the total analytical concentrations of calcium, magnesium, strontium, sodium, potassium, bicarbonate, carbonate, sulfate, fluoride, silica, sulfide, and chloride.

Samples of sediments were obtained in the fall of 1966 at a cross section below the convergence of the two rivers. The results of X-ray diffraction studies showed montmorillonite, kaolinite, illite, quartz, and calcite in all samples. Similar X-ray diffraction studies of suspended solids samples showed all these components except calcite (Falls, 1969).

Most of the methods used for the analytical concentrations in water samples were similar in substance to those in APHA Standard Methods (1965). Suspended matter was determined using the gravimetric method developed by Banse et al. (1965). Dissolved oxygen was determined using the Alsterberg (Azide) modification of the Winkler method on samples taken until September 1967; and the remaining values were obtained in situ using a Precision Scientific galvanic cell oxygen analyzer. Sodium, potassium, and strontium were determined by atomic absorption spectrophotometric procedures using a Perkin-Elmer Model 303 spectrophotometer (Fishman and Downs,

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Table I. Equilibrium Reactions and Stability Constants Involving Dissolved Components

Reaction	Stability constant, K =	Log K[a]
$CO_2 + H_2O = H_2CO_3^{=}$ [b]	$\{H_2CO_3^{=}\}/\{CO_2\}$	$-540.0/T - 0.777$[c]
$HCO_3^- + H^+ = H_2CO_3^0$	$\{H_2CO_3\}/\{H^+\}\{HCO_3^-\}$	$+630.0/T + 4.238$[c]
$CO_3^{2-} + H^+ = HCO_3^-$	$\{HCO_3^-\}/\{H^+\}\{CO_3^{2-}\}$	$+860.0/T + 7.447$[c]
$Ca^{2+} + HCO_3^- = CaHCO_3^+$	$\{CaHCO_3^+\}/\{Ca^{2+}\}\{HCO_3^-\}$	$+1.26$[b]
$Ca^{2+} + CO_3^{2-} = CaCO_3^0$	$\{CaCO_3^0\}/\{Ca^{2+}\}\{CO_3^{2-}\}$	$+3.20$[b]
$Mg^{2+} + HCO_3^- = MgHCO_3^+$	$\{MgHCO_3^+\}/\{Mg^{2+}\}\{HCO_3^-\}$	$+1.16$[b]
$Mg^{2+} + CO_3^- = MgCO_3^0$	$\{MgCO_3^0\}/\{Mg^{2+}\}\{CO_3^{2-}\}$	$+3.40$[b]
$Na^+ + HCO_3^- = NaHCO_3^0$	$\{NaHCO_3^0\}/\{Na^+\}\{HCO_3^-\}$	-0.25[b]
$Na^+ + CO_3^{2-} = NaCO_3^-$	$\{NaCO_3^-\}/\{Na^+\}\{CO_3^{2-}\}$	$+1.27$[b]
$Ca^{2+} + SO_4^{2-} = CaSO_4^0$	$\{CaSO_4^0\}/\{Ca^{2+}\}\{SO_4^{2-}\}$	$-292.7/T + 3.288$[c]
$Mg^{2+} + SO_4^{2-} = MgSO_4^0$	$\{MgSO_4^0\}/\{Mg^{2+}\}\{SO_4^{2-}\}$	$-1190.5/T + 6.350$[c]
$Na^+ + SO_4^{2-} = NaSO_4^-$	$\{NaSO_4^-\}/\{Na^+\}\{SO_4^{2-}\}$	$+0.72$[b]
$K^+ + SO_4^{2-} = KSO_4^-$	$\{KSO_4^-\}/\{K^+\}\{SO_4^{2-}\}$	$-673.6/T + 3.106$[d]
$H^+ + HS^- = H_2S$	$\{H_2S\}/\{H^+\}\{HS^-\}$	$+1500./T + 1.932$[c]
$H^+ + S^{2-} = HS^-$	$\{HS^-\}/\{H^+\}\{S^{2-}\}$	$+1470./T + 7.911$[c]
$H^+ + H_3SiO_4^- = H_4SiO_4^0$	$\{H_4SiO_4^0\}/\{H_3SiO_4^-\}$	$+9.7$[b]
$Mg^{2+} + F^- = MgF^+$	$\{MgF^+\}/\{Mg^{2+}\}\{F^-\}$	$+1.82$[b]

[a] T = temperature, °K. [b] Sillen and Martell, 1964. [c] Hostetler et al., 1967. [d] $H_2CO_3^{=}$ = true H_2CO_3; $[H_2CO_3] = [CO_2] + [H_2CO_3^{=}]$.

1966). Fluoride was determined using a fluoride ion sensitive electrode (Frant and Ross, 1966).

The concentrations and activities of all chemical species (ions and ion pairs) which make up a percent or so of the total analytical concentration of the major components were determined from the stability constants and estimates of the activity coefficients. The procedure used was a modification of that of Garrels and Thompson (1962), but more complete. It included more components, it considered temperature variations, it considered variations in ionic strength, and it applied more exacting mathematical techniques.

The equilibrium reactions and the stability constants used in the calculations are given in Table I. Some complexes were not included because of insufficient data to indicate their importance. However, the evaluation of the available data suggests that the components included made up more than 99% of the dissolved solids.

Equilibria of the Natural Waters of Lake Keystone

The essentials for formulation of equilibrium models have been reviewed by Morgan (1967). The assumption is made that the composition of water is governed by chemical reactions between the gas, liquid, and solid phases

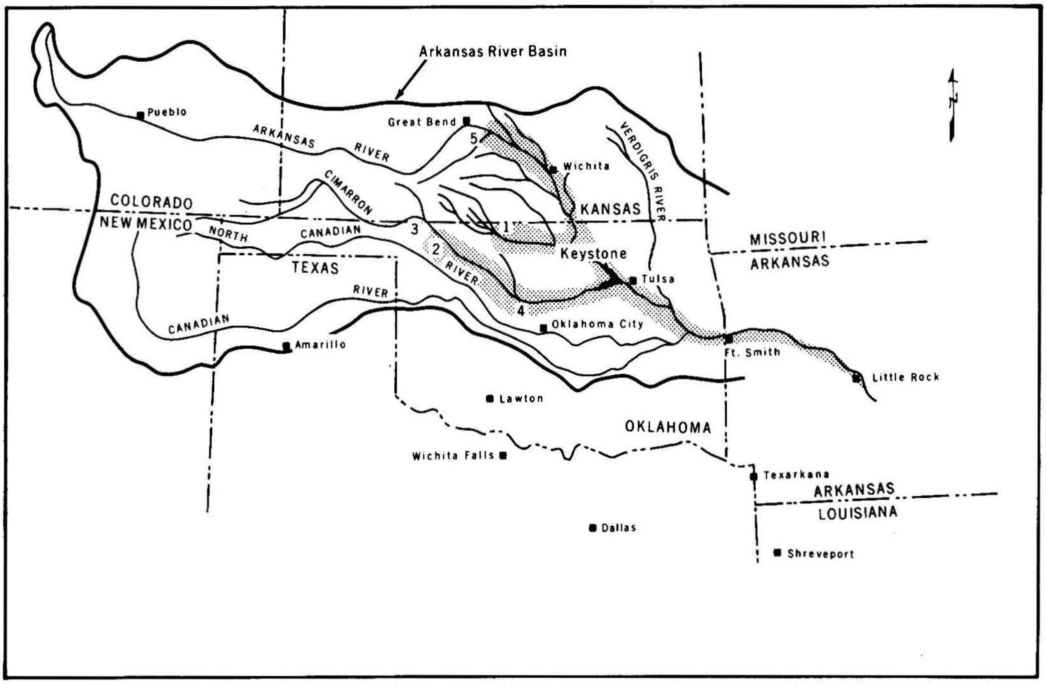

Figure 1. Arkansas River drainage basin showing the location of Lake Keystone. Numbers indicate areas of natural brine emissions. Shaded areas indicate brine affected streams.

that make up the systems at various stages in the hydrological cycle and that these reactions are rapid enough to approach a state of equilibrium within the average lifetime of the system. The process is visualized as a hypothetical experiment in which the phases which are to model the system are mixed together and allowed to react until a state of chemical equilibrium is attained. With equilibrium assumed, the composition variables or the activities of the dissolved components are calculated using available thermochemical data. The models are then compared to the real systems.

Before the heterogeneous equilibria of a natural water system can be considered, however, the various phases that the waters are in contact with and have contacted during their passage must be defined in some manner. One approach is to reconstruct the history of the waters.

Even though the minerals and mineraloids which make up lake sediments, bedrocks, soils, and suspended solids

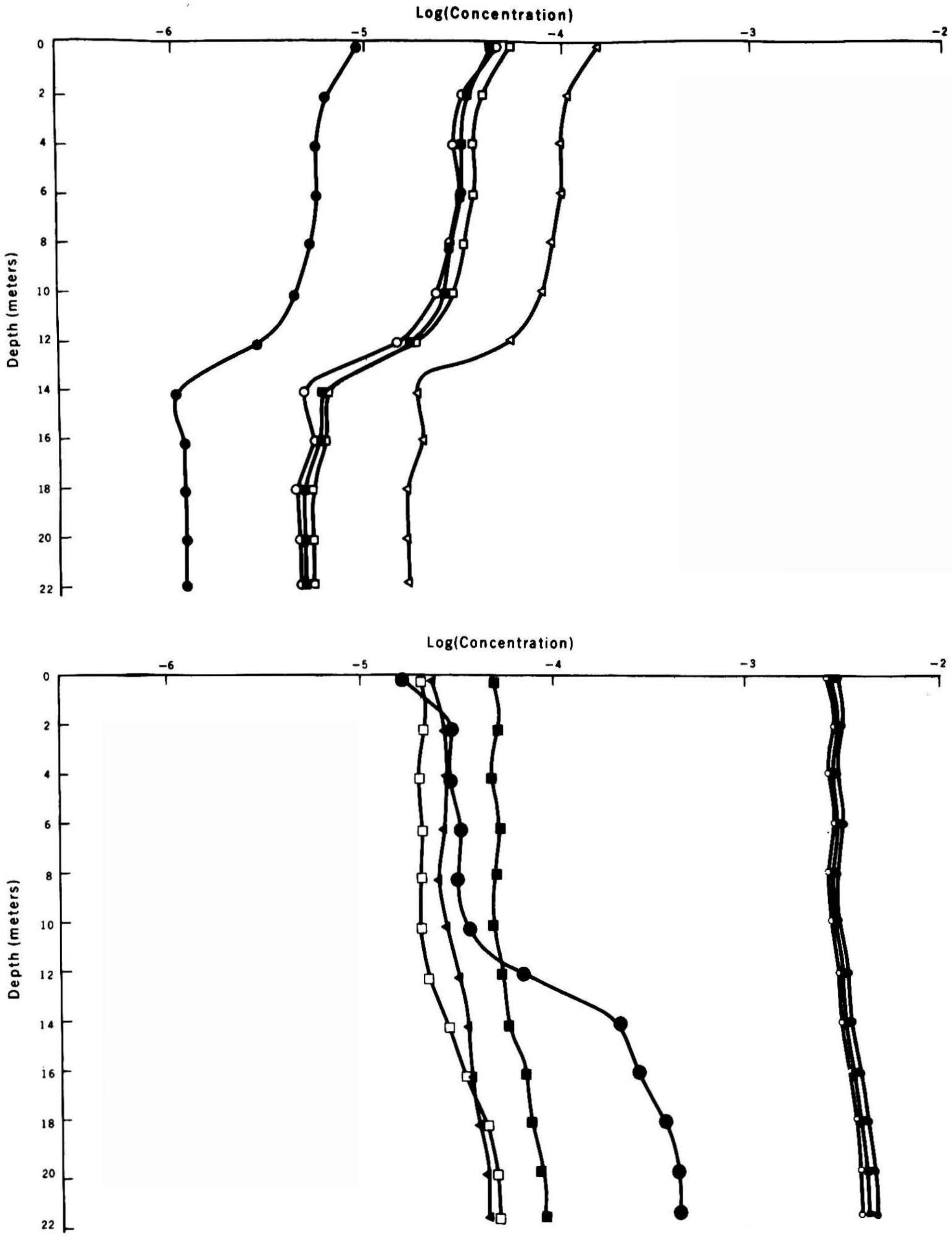

Figure 2. Distribution of dissolved carbonates at a time of chemical stratification (August 20, 1966)

• Total carbonates, • $NaCO_3^-$, ● CO_2, HCO_3^-, O $CaCO_3^\circ$, ■ Total HCO_3^-, ▲ $MgHCO_3^+$, △ Total CO_3^{2-}, □ CO_3^{2-}, ■ $MgCO_3^\circ$, ■ $CaHCO_3^+$, □ $NaHCO_3^\circ$

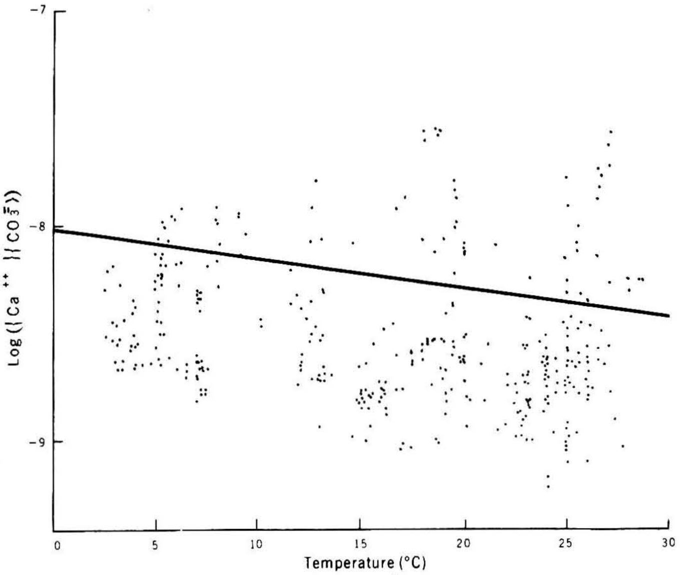

Figure 3. Ion activity product data for calcite in Lake Keystone. The solid line gives the saturation condition (Larson and Buswell, 1942)

are frequently ill-defined and may be very complex, well-known minerals with well-established chemical formulas were used to represent the solid phases in this study. Their definition was based on the geologic setting, the bedrock and soil mineralogy of the drainage basin (Jordan, 1967), X-ray diffraction studies, and established principles of the chemistry of minerals. From these studies, and from comparisons of flow rate data (Eley, 1970) and total chloride ion concentrations during the 1967 season, it appeared that the waters entering Lake Keystone were of at least two origins. One type originated in the area where the Permian formation is exposed at the surface in western Oklahoma and south-central Kansas. Here, the ground waters and surface waters contact large quantities of the minerals associated with chemical sedimentary rocks as well as the abundant silicate minerals in the shales and soils.

As the waters from this region drain into the main streams, they mix with waters which originate from areas where the highly soluble sedimentary rocks are not abundant. In the Rocky Mountains, the waters acquire their chemical properties primarily by the weathering of igneous rocks. The rocks and soils between the Rocky Mountains and the area of the Permian rocks are mainly sandstone, siltstone, and caliche.

The waters from these two areas continue to mix until they reach the head of the reservoir. In the area of the reservoir itself, rocks of the Pennsylvanian geological era occur at the surface. These are primarily shales composed of clay minerals, but limestone minerals are widely abundant.

The waters entering the reservoir carry relatively large loads of suspended solids. For example, one of the justifications for construction of Keystone Dam was to form a settling basin for the suspended solids of the Arkansas and Cimarron Rivers to minimize silting of the navigation channel downstream. These suspended solids are primarily degraded clay minerals (Falls, 1969).

Based on this description, the following hypothesis was to be tested: Waters originating in the area where the Permian rocks occur acquire their chemical composition by the dissolution of the common chemical evaporites, such as gypsum, calcite, dolomite, and halite and by dissolution or incongruent reactions of the clay minerals such as kaolinite, montmorillonite, and illite. Waters from this region then are diluted by fresher waters, mainly those originating from the western part of the drainage basin. The waters then contact a new group of solid phases which are present as suspended solids and the stream bed. These materials are composed mainly of the degraded clay minerals and calcite. As these waters flow down the rivers into the reservoir, they are mixed with the suspended solids and with lake sediments, and congruent as well as incongruent reactions continue to occur until equilibrium is approached.

Equilibrium Reactions

Carbonate System. The carbonates are derived mainly from the carbonate minerals and the atmosphere. Calcite is the thermodynamically stable form of calcium carbonate and appears to be the most important in fresh water systems. Argonite, however, is composed of a large amount of recent sediments and may be deposited under conditions in which calcite is the stable phase. The solution and precipitation of calcite appears to be rapid, and it has been observed to precipitate in lakes (Smith, 1960). It was also observed in the sediment samples from Lake Keystone. The distribution of dissolved carbonates in the solution phase, illustrated in Figure 2 was measured when the hypolimnion was anoxic due to chemical stratification (Eley et al., 1967).

Values of the activity product calculated from the analytical data, $\{Ca^{2+}\}\ \{CO_3{}^{2-}\}$, are plotted in Figure 3 as a function of temperature. Although there is considerable scatter, the points fall around the theoretical values for saturation with calcite. Most of the samples were undersaturated. Magnesium is generally associated with carbonates, and like calcium carbonate, there are several different forms found in nature. Although Bricker and Garrels (1967) show that the precipitation of magnesium carbonates, including dolomite, is very rare in fresh waters, the data of Hsu (1963) indicate that the dissolution process for dolomite in nature can approach the equilibrium condition and may be very important in controlling the water

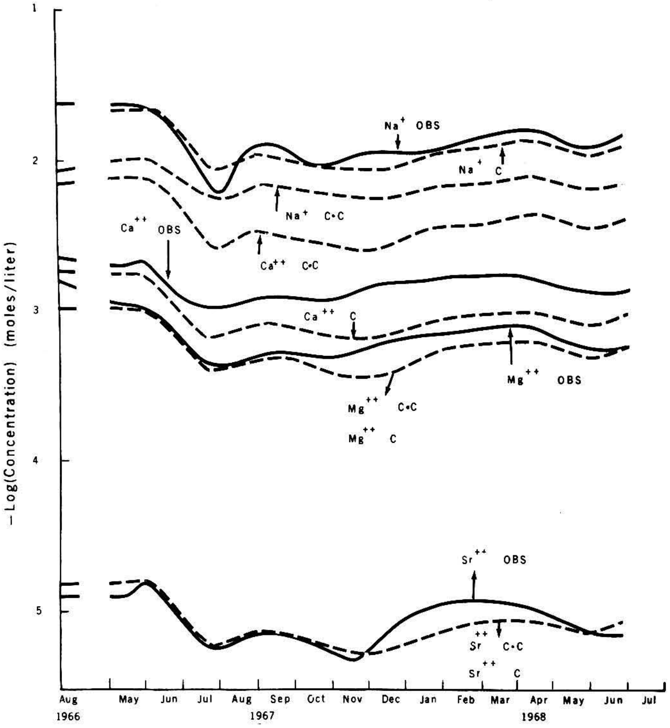

Figure 4. Comparison of observed concentrations of major cations with the variable dilution model

Subscripts OBS, C—C, and C refer to the observed, clay-calcite model, and clay model. $P(CO_2) = 10^{-2.9}$ atm

composition. The constants of Table II predict the activity ratio $\{Mg^{2+}\}/\{Ca^{2+}\} = 10^{-0.23}$ at equilibrium, while the observed ratio (Figure 4) was closer to $10^{-0.4}$ during much of the period measured, indicating undersaturation with respect to dolomite. Strontium carbonate, also, is commonly associated with carbonate sediments. In seawater, strontium partially replaces calcium in the aragonite structure and plays a major role in carbonate chemistry. In Lake Keystone, activity products both for $\{Ca^{2+}\}\{Mg^{2+}\}\{CO_3^{2-}\}^2$ and $\{Sr^{2+}\}\{CO_3^{2-}\}$ indicated undersaturation (Falls, 1969).

Chloride System. The chlorides formed no significant amounts of complexes with the cations considered here. In this system, they originated primarily from the solution of halite. Equilibrium with halite is the only reaction which would limit its concentration in natural water systems; but saturation with respect to halite was not observed in Lake Keystone.

Table II. Thermochemical Data and Equations Used to Develop Chemical Equilibrium Models

Reactions and Equations	
$H_2O = H^+ + OH^-$	$\{OH^-\}\{H^+\} = 10^{-14.35}$[a]
$CO_{2(g)} + H_2O = H_2CO_3$	$\{H_2CO_3\}/P(CO_2) = 10^{-1.33}$[b]
$HCO_3^- + H^+ = H_2CO_3$	$\{H_2CO_3\}/\{HCO_3^-\}\{H^+\} = 10^{6.42}$[c]
$CO_3^{2-} + H^+ = HCO_3^-$	$\{HCO_3^-\}/\{H^+\}\{CO_3^{2-}\} = 10^{10.43}$[d]
$CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$	$\{Ca^{2+}\}\{CO_3^{2-}\} = 10^{-8.22}$[e]
$CaMg(CO_3)_{2(s)} = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	$\{Ca^{2+}\}\{Mg^{2+}\}\{CO_3^{2-}\}^2 = 10^{-16.67}$[f]
$CaSO_4 \cdot 2H_2O_{(s)} = Ca^{2+} + SO_4^{2-} + 2H_2O$	$\{Ca^{2+}\}\{SO_4^{2-}\} = 10^{-4.44}$[g]
$SrSO_{4(s)} = Sr^{2+} + SO_4^{2-}$	$\{Sr^{2+}\}\{SO_4^{2-}\} = 10^{-6.5}$[h]
3Na-montmorillonite$_{(s)}$ $+ 2H^+ + 8H_2O$ = 4kaolinite$_{(s)}$ $+ 2H_4SiO_4 + 2Na^+$	$\dfrac{\{Na^+\}\{H_4SiO_4\}}{\{H^+\}} = 10^{4}$[i]
6Ca-montmorillonite$_{(s)}$ $+ 23H_2O + 2H^+$ = 7kaolinite $+ Ca^{2+} + 8H_4SiO_4$	$\dfrac{\{Ca^{2+}\}\{H_4SiO_4\}^8}{\{H^+\}^2} = 10^{-15.4}$[j]
$\{A^z\} = 0.5[A^z],\ Z = \pm 2$	
$\{A^z\} = 0.8[A^z],\ Z = \pm 1$	
$\{A^z\} = 1.0[A^z],\ Z = 0$	
$2([Ca^{2+}] + [Mg^{2+}] + [Sr^{2+}]) + [Na^+] + [H^+] = 2([CO_3^{2-}] + [SO_4^{2-}])$ $+ [HCO_3^-] + [OH^-] + [Cl^-]$	
Temperature = 15°C	

[a] Harned and Owen, 1958. [b] Markam and Kobe, 1941. [c] Harned and Bonner, 1945. [d] Harned and Scholes, 1941. [e] Larson and Buswell, 1942. [f] Kramer, 1967. [g] Latimer, 1952. [h] Sillen and Martell, 1964. [i] Feth et al., 1964. [j] Stumm and Leckie, 1967.

Sulfate System. The distribution of the various sulfate species in the solution phase is illustrated in Figure 5 for data from August 20, 1966. About 80% of the total sulfate occurred as the free sulfate ion.

Most of the sulfate in Lake Keystone is derived from the solution of gypsum from the Permian red beds, and these waters are diluted to varying degrees before they enter the reservoir. An evaluation of the activity product, $\{Ca^{2+}\}\ \{SO_4{}^{2-}\}$, obtained from the analyses showed, as expected, that the waters were far from saturation.

Strontium sulfate would be expected to be associated with the gypsum deposits. The waters of the reservoir, like gypsum, were far from saturation with respect to strontium sulfate.

Silicate System. The nature of aluminum silicate minerals in water systems is not adequately known. However, if simplified formulas for the aluminum silicate minerals are assumed to represent what must be highly complex, naturally occurring minerals, enough data are available to derive some useful stability relations.

Predominance diagrams or stability diagrams compiled from chemical thermodynamic data are useful in understanding the silicate reactions. The diagrams are prepared by writing the equations for the more probable transitions between the minerals and then balancing them by assuming that aluminum is conserved in the solid phase. The cations and $H_4SiO_4{}^{\circ}$ are added to conserve electric neutrality and the elements. The equilibrium constants are calculated from the free energy of formation of the constituents involved in the reaction.

Three systems were tested, Na_2O-Al_2O_3-SiO_2-H_2O, K_2O-Al_2O_3-SiO_2-H_2O, and CaO-Al_2O_3-SiO_2-H_2O. The data from Lake Keystone, in all three systems, fell primarily within the stability field of kaolinite near the kaolinite-montmorillonite boundary (Falls, 1969).

Equilibrium Models

Several equilibrium models were developed based on the history of the waters of Lake Keystone. These were designated as an evaporite, a diluted clay-calcite, a diluted clay, a variable dilution clay-calcite, and a variable dilution clay model. In all models, ten components were specified: H_2O, CO_2, HCl, CaO, MgO, SrO, Na_2O, SO_2, SiO_2, and Al_2O_3.

The evaporite model simulated conditions in the area of the Permian formations. The nine phases used to reconstruct the system were gypsum, dolomite, calcite, strontium sulfate, kaolinite, sodium montmorillonite, calcium montmorillonite, the solution, and air containing variable amounts of carbon dioxide to test the effect of supersaturation.

For this model system containing 10 components and 9 phases, three independent variables were chosen to satisfy Gibbs phase rule. These were the average temperature of the water, 15°C, a pressure of 1 atm, and a chloride ion concentration of $10^{-1.5}M$, values representative for streams in this area (Love, 1966). The equilibrium data, activity coefficients, and the equation for the charge balance are given in Table II. There are notable variations in the available values for the equilibrium constants, especially for the silicate minerals. In all cases, the values were chosen to be consistent with previous work in these laboratories and with those used by other workers.

The system of equations was solved by combining the equations for the individual equilibrium constants to obtain the activities of the individual components in terms of the activities of the hydrogen ion and the partial pressure of carbon dioxide. Ion pairs were not included in the treatment. Activities were converted to concentrations, and these were combined into the equation for electroneutrality of Table II to give a higher degree polynomial equation containing only one unknown, the hydrogen ion. This equation was solved using Newton's approximation method (Butler, 1964).

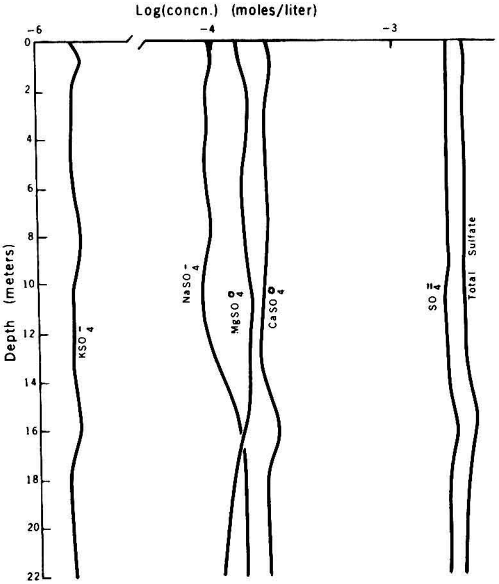

Figure 5. Distribution of dissolved sulfates at a time of chemical stratification (Aug. 20, 1966)

For example, the equations of Table II were combined and both sides multiplied by $\{H^+\}^2$ to obtain:

$$\frac{4}{P(CO_2)}(10^{9.96} + 10^{9.73} + 10^{7.90})\{H^+\}^4 +$$

$$1.25\left(1 + \frac{10^{5.17}}{P(CO_2)^{0.125}}\right)\{H^+\}^3 = [Cl^-]\{H^+\}^2 +$$

$$1.25(10^{-14.35} + 10^{-7.75}P(CO_2)\{H^+\} +$$

$$4P(CO_2)(10^{-18.18} + 10^{-14.40})\} \quad (1)$$

The equation was solved for the activity of the hydrogen ion at several values of $P(CO_2)$, and the remaining concentrations were then calculated. The results (Falls, 1969), when compared with the data of Love (1966) for surface waters in this area, indicated that the more saline waters differ from those predicted by the model by only a few tenths of a log unit or less.

For the diluted clay-calcite model, it was assumed that the waters from the evaporite minerals were diluted by waters originating upstream from the Permian formation. The water phase then was mixed with the clay minerals and calcite which were present in the suspended solids, the soils, the stream beds, and the reservoir basin.

The model was prepared by removing the solution phase of the evaporite model, diluting it by an appropriate amount, mixing it with the clay minerals and calcite, and exposing it to air containing carbon dioxide. Equilibrium was imposed, and the composition variables were calculated using a procedure similar to that used in the evaporite model. Reactions involving sulfate such as the sulfide formation actually observed during the early history of the reservoir (Eley et al., 1967; Falls, 1969) were assumed to be negligible in these studies.

Six phases were specified: solution, atmosphere, calcite, sodium montmorillonite, calcium montmorillonite, and kaolinite. With 10 components, six variables were specified to define the system: temperature = 15°C, pressure = one atmosphere, $(Cl^-) = 10^{-1.91}M$, $(SO_4^{2-}) = 10^{-2.99}M$, $(Mg^{2+}) = 10^{-3.24}M$, and $(Sr^{2+}) = 10^{-5.07}M$. The degree of dilution was based on the concentration of sulfate predicted by the evaporite model ($10^{-1.9}M$) and the average observed value in the reservoir during this study ($10^{-2.99}M$). This gave a dilution factor of $10^{-1.08}$. The solution phase from an evaporite model with a carbon dioxide partial pressure of $10^{-2.25}$ atm was used (Falls, 1969).

Proceeding as in the evaporite model, the final form of the equation was:

$$\frac{4}{P(CO_2)}10^{9.96}\{H^+\}^4 + 1.25\left(1 + \frac{10^{5.17}}{P(CO_2)^{0.125}}\right)\{H^+\}^3 =$$

$$[2(-10^{-3.24} - 10^{-5.07} + 10^{-2.99}) + 10^{-1.90}]\{H^+\}^2 +$$

$$1.25[10^{-14.35} + 10^{-7.75}P(CO_2)]\{H^+\} + 4(10^{-18.18})P(CO_2) \quad (2)$$

Equation 2 was solved for the hydrogen ion activity at several partial pressures of carbon dioxide by Newton's approximation method, and the results were substituted into the original equations to obtain the remaining unknown activities and concentrations. At a partial pressure of carbon dioxide representative of that of natural waters and of Lake Keystone, the agreement between calculated and observed solution concentrations was excellent (Falls, 1969).

Diluted Clay Model. The X-ray diffraction studies of the reservoir (Falls, 1969) suggested that calcite was very abundant in the sediments but not in the suspended matter. In addition, the comparison of the solubility product of calcite with that observed in the reservoir (Figure 3) suggested that the waters were usually undersaturated with respect to calcite. Although the results of the diluted clay–calcite model were not unreasonable, the values predicted for the calcium concentration by the model were about 0.3 logarithm unit high. To examine the possibility of the insignificant contribution of calcite to the system, a model was investigated using only five phases: solution, atmosphere, kaolinite, sodium montmorillonite, and calcium montmorillonite.

With the same 10 components as before, seven variables were specified to define the system. Temperature, pressure, and the concentration of magnesium, strontium, sulfate, and chloride were fixed at the values: 15°C, one atmosphere, $10^{-3.24}$, $10^{-5.07}$, $10^{-2.99}$, and $10^{-1.90}M$, respectively, as in the diluted calcite–clay model. Calcium was chosen as the seventh variable. When we use the same dilution factor, $(Ca^{2+}) = 10^{-2.85}M$. From the data of Table II, Equation 3 was obtained and solved as before.

$$1.25\left[1 + \frac{10^{5.15}}{P(CO_2)^{0.125}}\{H^+\}^3\right] =$$

$$[2(-10^{-3.24} - 10^{-2.85} - 10^{-5.07} + 10^{-2.99}) + 10^{-1.9}]\{H^+\}^2 +$$

$$1.25[10^{-14.35} + 10^{-7.75}P(CO_2)]\{H^+\} + 4(10^{-18.18})P(CO_2) \quad (3)$$

The results are tabulated by Falls (1969)

Variable Dilution Clay-Calcite Model. The degree that the waters from the Permian basin are diluted will vary depending on the amount of precipitation and runoff. The variable dilution clay–calcite model was developed to allow the degree of dilution to be specified at times which corresponded to times of observation of the reservoir properties.

The construction of the model involved: the formulation of an evaporite model, as above, using the same partial pressure of carbon dioxide, dilution of the solution phase from the evaporite model by different amounts to simulate the differing degrees of dilution at given times, and, finally, the formulation of the model using the concentrations of magnesium, strontium, and sulfate defined by the first two steps.

Assuming that the chloride ion concentrations in the waters in contact with the evaporite minerals were proportional to the other dissolved constituents, a dilution factor was derived based on the chloride ion concentration. When the previously derived dilution factor of $10^{-1.08}$ was applied to the average observed chloride concentration, $10^{-1.90}M$, an apparent chloride saturation value of $10^{-0.82}M$ was obtained. This factor was used in the proportionality equation,

$$[X] = \frac{[Cl_{obs}^-]}{10^{-0.82}}[X_{sat}] \quad (4)$$

from which the concentrations of magnesium, strontium, and sulfate were calculated for the diluted phase of the system. The quantity $[X]$ was the concentrations of magnesium, strontium, or sulfate after dilution, $[X_{sat}]$ was the corresponding concentration predicted from the evaporite model, and $[Cl^-_{obsd}]$ was the observed chloride concentration at the particular time that the system of Lake Keystone was to be modeled.

The computation procedures were the same as used above. To evaluate the effect of the suggested supersaturation with respect to carbon dioxide, the calculations were performed at several values of $P(CO_2)$. The values of the average observed monthly concentrations of some of the major ions as well as the values predicted by the model are plotted in Figures 4 and 6.

Variable Dilution Clay Model. In the same manner as the variable dilution clay–calcite model, a model similar to the diluted clay model was prepared by allowing the degree of dilution to vary. The same dilution factors used in the variable dilution clay–calcite model were applied to Ca^{2+}, Mg^{2+}, Sr^{2+}, and SO_4^{2-}. The remaining specified variables were unchanged. The results are plotted in Figures 4 and 6.

Discussion

When we consider the state of our knowledge of the solution chemistry of sedimentary minerals under natural conditions, and the limitations on our ability to define by analysis the water chemistry of an impoundment as large as Lake Keystone, the agreement between the observed data and either the clay–calcite model or the clay model was quite good. The data agreed best with the clay model, but the widespread occurrence of calcite in the system would suggest that the clay–calcite model would be the one most likely to be approached. The results indicated that the composition of the waters was determined by definite chemical reactions, which included the solid phases, that were rapid enough to approach a state of chemical

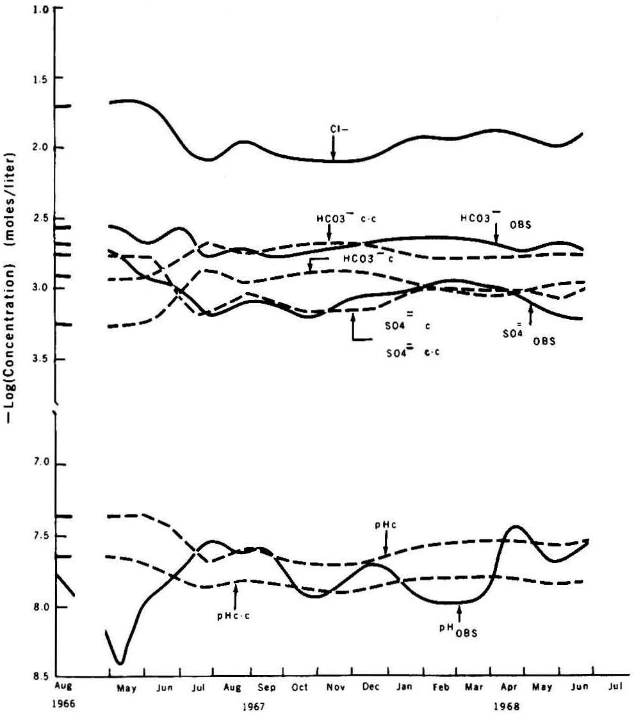

Figure 6. Comparison of observed concentrations of major anions and pH with concentrations calculated from the variable dilution equilibrium models

Subscripts C—C, C, and OBS refer to clay-calcite model, clay model, and observed values. $P(CO_2) = 10^{-2.9}$ atm

equilibrium. There was no indication that the composition of the waters was determined merely by chance.

Equilibrium between the carbon dioxide in air and the solution did not appear to be a good assumption. In the analyses, a series of solutions using several partial pressures of carbon dioxide in the gas phase were used to allow for this consequence. Another manner to express this effect, and perhaps a more correct way, would be to remove the gas phase from the model and specify the partial pressure of carbon dioxide in the solution phase. The same end result would be obtained.

The concentrations of sulfate, magnesium, and strontium were modeled quite well by the dilution treatments. Not only did the absolute values agree well, but the general trends were followed quite closely.

Calcium concentrations predicted by the clay-calcite model were higher than the observed values, while those specified by dilution in the clay model were lower. The assumption in the clay model was that the calcium concentration in the waters was determined chiefly by the calcium added to the waters from the Permian formation; and since the hydrogen ion concentration was negligible compared to the calcium ion concentration, the ion exchange reaction would not influence the calcium concentration significantly. However, there is "fixed acid" present in the carbonate and silicate systems. This could have been responsible for the low calcium values calculated by the clay model.

If the calcium concentration were equated to that observed in the reservoir, higher bicarbonate and lower sodium and hydrogen concentrations would be predicted by the clay model. The actual situation would be expected to be somewhere between these two models; but the clay-calcite model should be approached more closely more of the time. The essential features of the trends predicted by the varying degrees of dilution were followed closely, however. Also, sodium montmorillonite and calcium montmorillonite were assumed to be two separate phases. It may have been more appropriate to count these as one phase.

All equilibrium treatments must be considered approximations since in natural water systems equilibrium is rarely obtained except in a dilution or dissolution process. The pH data of Figure 6, for instance, suggests the expected seasonal variation in acidity due to photosynthesis, a process not considered here. Although many of the microprocesses may be blurred by this type of treatment, the results are necessary to the development of any dynamic model designed to study chemical reactions in the system.

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Kinetic Study of Phosphate Reaction with Aluminum Oxide and Kaolinite

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■ The reaction of aqueous phosphate ($\sim 3 \times 10^{-4}M$) with alumina and kaolinite shows a rapid (12–24 hr) adsorption step followed by a slow process, obeying a first-order rate law, which extends over the next 60 days and probably involves nucleation and growth of a hexagonal $AlPO_4$ phase. For kaolinite with 10.7 m^2/g surface area, solids concentration 7.5 g/l, pH = 4.6, as well as for α-Al_2O_3 with surface area 10 m^2/g, solids concentration 2.5 g/l, and pH = 4.3, the first-order rate constant at 50°C is 0.022 day^{-1}. Increasing temperature increases the rate, with an activation energy of 2.4 Kcal/mol. Addition of fluoride ion ($10^{-4}M$) decreases the amount of phosphate initially adsorbed but does not affect the first-order rate. The rate constant increases proportionally to the solid surface available, and decreases with increasing pH to essentially zero at pH ≥ 7. Successive addition of phosphate aliquots to the same sample of solid uses up the sites available for the rapid initial step but does not strongly influence the rate of the slow step.

Phosphorus has been recognized as one of the main nutrients which accelerates the process of eutrophication. Sediments of water systems participate directly or indirectly in the cycle of nutrients and are a possible source of nutrients for undesirable algae and aquatic plant growth. The high phosphorus-binding capacity of sediments is correlated with high clay mineral content of the sediment (Livingstone and Boykin, 1962; Frink, 1969). Leckie (1969; Leckie and Stumm, 1970; Stumm and Leckie, 1971) has investigated the kinetics of phosphate fixation by Ca^{2+} in the presence of calcite. Although numerous studies have investigated the removal of phosphate from solution by soils, aluminum oxides, and iron oxides (Hemwall, 1957a; Kittrick and Jackson, 1955, 1956; Hsu, 1964, 1965), notably lacking are quantitative kinetic studies on the precipitation of phosphate by reaction with clay minerals at phosphate concentrations (10^{-7}–$10^{-4}M$) and temperatures (10–25°C) corresponding to natural waters. Because the reaction of phosphate with kaolinite is related to the alumina content of the kaolinite, the kinetics of the reaction of phosphate with aluminum oxide may give a good insight into the alumina contribution to the phosphate reactions with kaolinite. A quantitative kinetic study at 25° and 50°C of the reaction of phosphate with clay minerals at relatively low phosphate concentrations ($\sim 10^{-4}M$) is presented in this paper and discussed in terms of its implications for phosphate exchange with sediments. These results provide a closer approximation to natural waters than presently available data, and represent a compromise between relevance and experimental precision.

Materials and Experimental Methods

The α-Al_2O_3 sample was obtained from the Linde Co., and had a uniform particle size of 0.3–1 μ. The kaolinite (No. 5, Lamar Pit, Barth, S.C.) sample was from Ward's Natural Science Establishment, Inc. (P.O. Box 1712, Rochester, N.Y. 14603). Its composition and properties have been published (Kerr et al., 1950) and verified recently (Maynard 1972). The kaolite sample was ground with a porcelain mortar and pestle, washed with distilled water, then dried at 105°C for 2 days. The dried sample was ground again and passed through a series of U.S. Standard sieves using a mechanical shaker. The particles

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of kaolinite less than 74 μ in size were used for the experiments. Such ground kaolinite is known to have an alumina-like reactivity (Swenson et al. 1949). Surface areas of α-Al_2O_3 and kaolinite samples were determined on a Perkin-Elmer Model 212D Sorptometer using nitrogen gas as the adsorbent. The α-Al_2O_3 and kaolinite samples were found to have specific surface areas of 10.0 and 10.7 m^2/g, respectively.

Aluminum orthophosphate crystal samples were obtained from British Drug House Ltd. and confirmed as metavariscite ($AlPO_4 \cdot 2H_2O$) by X-ray diffraction.

All solutions and suspensions were prepared with distilled water and reagent grade chemicals; pH values were measured with a Beckman Model G pH meter, employing a Fisher combination electrode.

The kinetic experiments were carried out in cylindrical, water-jacketed reaction vessels covered with lucite plates to prevent loss of water vapor. Mixing was done by magnetic stirrers. The contents of the reaction vessels were maintained at constant temperature (±0.3°C) by circulation of water through the jacket. A constant-temperature water bath (Ultrathermostat) was used to control the water temperature.

A known volume of distilled water was placed in the reaction vessel and a predetermined amount of α-Al_2O_3 or kaolinite was added. The suspension was kept at constant temperature and was continuously mixed by a magnetic stirrer. The pH was adjusted by HCl or NaOH to the desired pH values and checked periodically. At least 2 days of equilibration time was allowed for all suspensions so that pH could be adequately stabilized. Additional reagents (e.g., F^-) were added half an hour prior to the addition of phosphate. The phosphate solution to be added to the reaction suspension was made from Na_2HPO_4 and NaH_2PO_4 in proportions so as not to affect the pH of the reaction suspension. Constant pH was maintained during the experiments by the addition of HCl or NaOH solution. Initially such adjustments were made frequently. When the rate of the reaction decreased, one pH adjustment per day was sufficient. Samples were withdrawn periodically and immediately filtered through 0.2-μ pore size Millipore filters. The phosphate concentration of the filtrate was determined by using a modified version of the molybdenum blue procedure (Murphy and Riley, 1962).

The aluminum concentrations in the solutions at different pH values were measured before the addition of phosphate and 1 week after. The samples were filtered through 0.2-μ Millipore filters, and the aluminum concentration in the filtrate was measured by a colorimetric method using aluminon reagent (Black, 1965).

Precipitates formed by the reaction of phosphate with α-Al_2O_3 and kaolinite were examined with a Hitachi Model HU-11 electron microscope. The samples were supported on 200-mesh carbon coated grids and were dried on Whatman filter paper for a few hours before examination.

All X-ray diffraction patterns for the identification of the materials were run on a Norelco unit utilizing Cu-K_α radiation. Further details of Experimental methods are given elsewhere (Chen, 1972).

Results

The kinetic data for phosphate reaction with α-Al_2O_3 and kaolinite at different pH values are shown in Figures 1 and 2, plotted on a semilog scale. The phosphate removal by α-Al_2O_3 and kaolinite was very rapid for the first 2 hr. For the period from 2–24 hr the rate of reaction decreased but was still relatively fast. After one day the reaction rate slowed appreciably, and the semilog plot was linear from then on. The rate of phosphate removal increased strongly as pH decreased.

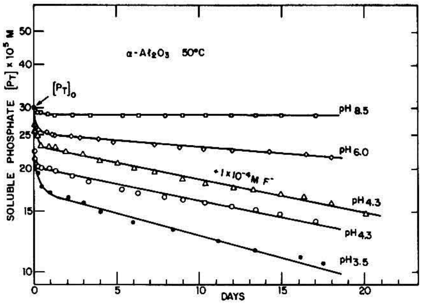

Figure 1. Kinetics of phosphate removal by α-Al_2O_3 at 50°C

Semilogarithmic plot is linear after the first 24 hr. Initial total phosphate $3 \times 10^{-4} M$, solids concentration 2.5 g/l. Note that addition of $10^{-4} M$ fluoride decreases the amount removed in the initial step but does not change the logarithmic rate

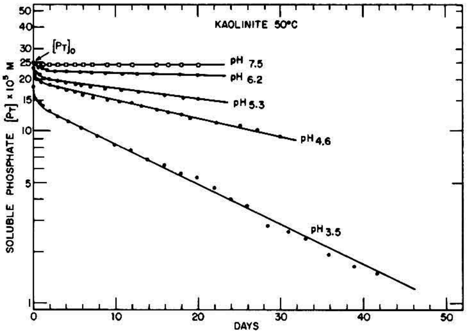

Figure 2. Kinetics of phosphate removal by Kaolinite at 50°C

Semilogarithmic plot is linear after the first 24 hr. Initial total phosphate $2.5 \times 10^{-4} M$, solids concentration 7.5 g/l.

At pH = 8.5 and initial total phosphate $(P_T)_0 = 3 \times 10^{-4} M$, no further phosphate was removed after one day of reaction time with α-Al_2O_3. Similarly, no further phosphate removal was observed after 1 day of reaction with kaolinite at pH = 7.5 and $(P_T)_0 = 2.5 \times 10^{-4} M$. The amount of phosphate removed during the initial 24-hr rapid phase increased as pH decreased. No maximum removal at pH ~4 was observed under these experimental conditions, in marked contrast to our previously published 25°C adsorption studies (Chen et al. 1973). This difference may be due to the different pre-equilibration time. At pH >6 the phosphate removed was comparable to that previously reported at 25°C.

Since reaction of phosphate with α-Al_2O_3 and kaolinite in acid solution in the slow reaction step can be approximately fitted by a linear semilog plot (Figures 1 and 2), the reaction can be described by the first-order form

$$-\frac{d(\mathrm{P})}{dt} = K_{\mathrm{obs}}(\mathrm{P}) \qquad (1)$$

where (P) is the total soluble phosphate and t is the reaction time. Values for K_{obs}, the observed specific rate constant, for different pH values and solids concentrations of aluminum oxide and kaolinite are given in Table I. There is no measurable reaction rate for pH >7.5. The alumi-

Table I. Phosphate Removal Kinetics

Observed specific rate constants in the following slow reaction step

Kaolinite (surface area, 10.7 m^2/g)				α-Al_2O_3 (surface area, 10 m^2/g)			
		K_{obs} (day^{-1}) at 50°C				K_{obs} (day^{-1})	
Solids concn, g/l.	pH	First phosphate addition	Second phosphate addition	Solids concn, g/l.	pH	At 50°C	At 25°C
7.5	3.5	0.0560	0.0587	2.5	3.5	0.0329	0.0240
7.5	4.6	0.0224		2.5	4.3	0.0219	
15.0	4.6	0.0398	0.0550	2.5[a]	4.3	0.0219	
7.5	5.3	0.0110		2.5	6.0	0.0071	
7.5	6.2	0.0030		2.5	8.5	0	
7.5	7.5	0					

[a] 1.0×10^{-4} M fluoride added.

Table II. Concentrations of Al and P in Solution after 7 Days

	$-\log [Al_T]$		$-\log [P_T]$		
pH	Before P addition	7 days after	7 days after[a]	pK_{so}[b]	$-\log (Al_T)$, for gibbsite[c]
α-Al_2O_3, 2.5 g/l., 50°C, $[P_T]_0 = 3 \times 10{-}^4M$					
3.5	4.74	4.85	3.86	19.73	(0.99)
4.3	5.60	5.70	3.77[d]	19.67	(3.32)
4.7	—	—	3.74[e]	—	4.42
6.0	7.	7.	3.62	19.5	6.64
7.2	6.3	—	—	—	5.50
8.5	4.51	4.50	3.55	(23.67)	4.20
Kaolinite 7.5 g/l., 50°C, $[P_T]_0 = 2.5 \times 10^{-4}M$					
3.5	4.5	4.93	4.01	19.96	(0.99)
4.6	5.95	6.10	3.80	19.80	(4.15)
5.3	6.8	6.8	3.74	19.89	5.91
6.2	7.	7.	3.66	20.4	6.48
7.5	5.50	5.45	3.62	(21.85)	5.20
Kaolinite 15 g/l., 50°C, $[P_T]_0 = 2.5 \times 10^{-4}M$					
4.6	5.70	5.86	3.98	19.74	(4.15)

[a] Interpolated from Figures 1 and 2.

[b] K_{so} calculated assuming the solid phase is $AlPO_4 \cdot nH_2O$ and the equilibrium constants (IUPAC Notation; Sillen and Martell, 1964, 1971) for Al hydrolysis: $^*K_1 = 10^{-5}$, $^*K_4 = 10^{-22.2}$; for H_3PO_4 dissociation: $pK_{a1} = 2.2$, $pK_{a2} = 7.2$, $pK_{\alpha 3} = 12.3$. Polymeric hydrolysis products and $AlPO_4$ complex species are neglected.

[c] Calculated assuming $^*K_{SO} = 10^{+9.5}$, $^*K_{s1} = 10^{+4.5}$, $^*K_{s4} = 10^{-12.7}$ (Sillen and Martell, 1964, 1971).

[d] The sample with $10^{-4}M$ F^- gave $-\log[P_T] = 3.70$ (A_T) was not determined.

[e] The sample with 0.1 g/l. meta-variscite gave $-\log[P]_T = 3.72$.

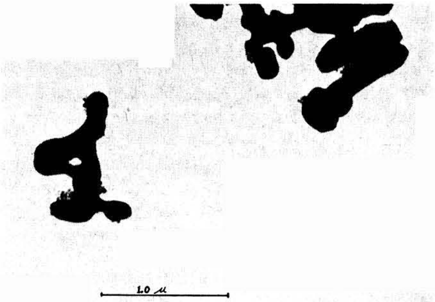

Figure 3. Electron micrograph of new solid phase (hexagonal crystal)

This sample resulted from the reaction of α-Al_2O_3 with $3 \times 10^{-4}M$ NaH_2PO_4 at pH = 4.3 for 18 days. The rounded dark particles are the original aluminum oxide

num concentrations at different pH values before, and one week after, the addition of phosphate are shown in Table II and compared with the concentration in equilibrium with aluminum phosphate or gibbsite. In the most acid solution (pH = 3.5) the aluminum concentration decreased somewhat after the addition of phosphate, but at higher pH the differences were nearly negligible. The total concentration of dissolved aluminum (originating from α-Al_2O_3 or kaolinite) was pH dependent, with values below the equilibrium solubility of gibbsite in all the solutions, but close to that for amorphous $Al(OH)_3$ in the alkaline solutions.

The formation of new hexagonal crystals was observed under the electron microscope after five days of reaction between phosphate and α-Al_2O_3. Figure 3 shows the formation process in acid solutions at 50°C and total phosphate concentration $3 \times 10^{-4}M$. No such new solid phase was found in the unphosphated α-Al_2O_3 control. The new solid exhibited larger size and multilayer growth as the phosphate concentration increased (Chen, 1972). These crystals are similar to those reported to form when kaolinite reacts with $1M$ phosphate (Kittrick and Jackson, 1956).

Crystals of the new solid phase were very thin ($\leq 0.02\ \mu$) and electron transmission diffraction proved impractical since the samples deteriorated due to the heat generated by the focused electron beam. Crystal lattice d spacings for the product of the reaction of α-Al_2O_3 with $1M$ NaH_2PO_4 were measured on a larger sample by X-ray diffraction, however, and the results are listed in Table III. The observed d spacings are compared with ASTM d spacings for α-Al_2O_3 and aluminum phosphate hydrate ($AlPO_4 \geq 2H_2O$). The observed d spacings of the sample are equivalent to superposition of the d spacings for α-Al_2O_3 and a product very similar to $AlPO_4 \geq 2H_2O$. In the kaolinite–phosphate system it was difficult to distinguish the new solid phase from kaolinite particles at low phosphate concentrations and for short reaction periods, because kaolinite particles also show some hexagonal shapes.

The effect of fluoride ($1 \times 10^{-4}M$) in decreasing the rate in the rapid initial step of phosphate removal by α-

Table III. Crystal Lattice *d* Spacings for the Product of Reaction of α-Al_2O_3 with $1M$ NaH_2PO_4 at pH 4.8, 50°C

(Reaction time; five months)

ASTM *d* spacings		Observed *d* spacings of α-Al_2O_3 reacted with $1M$ NaH_2PO_4 after five months[b]
α-Al_2O_3	$AlPO_4 \cdot \geq 2H_2O$[a]	
	16.5	16.46
	3.93	3.85
3.479		3.48
	3.28	
		3.16
		2.84
2.552		2.558
2.379		2.384
2.085		2.086
1.740		1.744
1.601		1.604
1.404		1.407
1.374		1.375

[a] *d* spacing at 16.5 is most intense.

[b] Although the *d* spacings of 2.84, 3.16 do not correspond exactly with 3.28, no compound other than $AlPO_4 \cdot \geq 2H_2O$ has as intense *d* spacings at 16.46 and 3.85 as that observed.

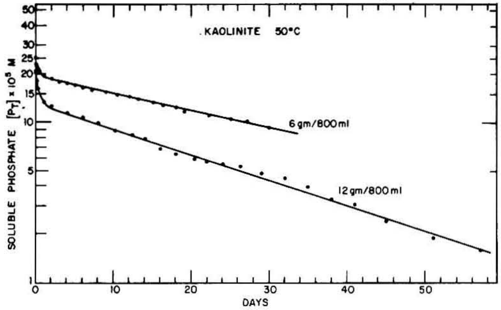

Figure 4. Effect of solids concentration on phosphate removal by kaolinite at 50°C

Initial total phosphate 2.5 × $10^{-4}M$, pH = 4.6

Al$_2$O$_3$ are shown in Figure 1. Fluoride did not affect the rate of phosphate removal in the following slow step (Table I).

The effect of surface area (or solids concentration) on the kinetics of phosphate removal by kaolinite for pH = 4.6 is shown in Figure 4 and Table I. Doubling the solids concentration of kaolinite caused the amount of phosphate removed during the initial 24 hr (rapid step) to increase twofold (from 4.7 × $10^{-5}M$ to 9.4 × $10^{-5}M$). These results indicate that the initial phosphate removal by kaolinite is proportional to the number of available surface sites. The rate of phosphate removal during the following slow step also increased when the surface area was doubled, but this increase was not quite a factor of two (K_{obs} changed from 0.0224 day^{-1} to 0.0398 day^{-1}).

The effect of temperature on the kinetics of phosphate removal by α-Al$_2$O$_3$ is shown in Figure 5. Examining these data reveals that there is no significant increase in phosphate removal during the first 24-hr rapid step as the temperature is raised from 25° to 50°C. The ratio of the observed first-order rate constants for the second step (K_{obs} at 50°/K_{obs} at 25°C) is 1.37, corresponding to an activation energy of 2.4 Kcal/mol.

The effect of successive additions at short time intervals of phosphate into the same sample of α-Al$_2$O$_3$ or kaolinite at 25°C is shown in Figures 6a and 6b. The amount of phosphate removal during the initial rapid step decreases with each addition of phosphate.

Figure 7 shows the results of successive additions of phosphate to kaolinite on a much longer time scale and at 50°C. This solution was at pH 4.6 with a solids concentration of 15 g/l. Similar results were obtained at pH 3.5 and 7.5 g/l. In Figure 7 the amount of phosphate removed in the second phosphate addition, during the 24-hr rapid step, was less than the amount removed in the first addition. The phosphate removal in the following slow step can be approximately fitted to first-order kinetics for each sequential phosphate addition. The increase in the observed specific rate constants in the second phosphate addition was more apparent in the kaolinite experiment with 15 g/l. solids concentration (Table I).

Since the X-ray studies had indicated that the new phase formed was close to some type of variscite, addition of crystals of meta-variscite might be expected to increase the number of nuclei and hence the rate of phosphate removal. The kinetic data for phosphate removal by α-Al$_2$O$_3$ at pH = 4.7 with the addition of meta-variscite crystals are shown in Figure 8. The rate of phosphate removal decreased as compared to the control α-Al$_2$O$_3$–phosphate system, an effect *opposite* from what was expected.

Discussion

The division of phosphate removal kinetics into a rapid step which is complete within 24 hr and a slower step which may continue for months afterward has been recognized by a number of workers. For example, Coleman (1944) noted that the removal of phosphate by montmorillonitic and kaolinitic clays at pH 3–5 continued for more than 1 month, Low and Black (1947) noted an increased amount of phosphorus fixed by kaolinite at pH 4.5 in 1 week as compared with 48 hr. Haseman et al. (1950) showed the rapid and slow steps, as well as the decrease in rate with increasing pH, in phosphate fixation by illite, montmorillonite, kaolinite, gibbsite, and goethite. Kittrick and Jackson (1955) pointed out that the rate of reaction of KH$_2$PO$_4$ with various soils decreased rapidly with time, Hemwall (1957b) demonstrated rapid uptake of phosphorus by kaolinite and montmorillonite at pH 4 during the first 4 hr and a slower uptake over the next 30 days. Hsu and Rennie (1962) obtained quantitative rates of uptake by amorphous alumina from a 40 ppm (1.3 × $10^{-3}M$) phosphate solution at pH 3.8 which correspond to

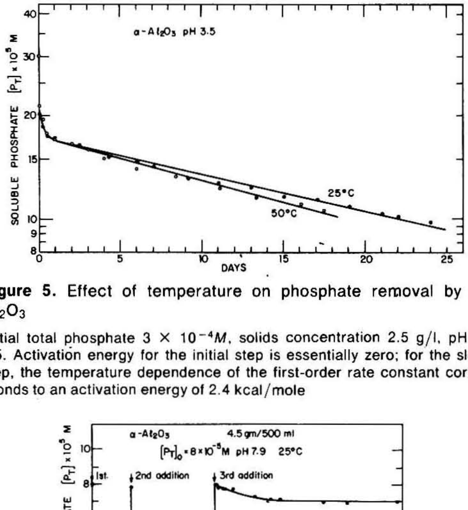

Figure 5. Effect of temperature on phosphate removal by α-Al$_2$O$_3$

Initial total phosphate 3 × $10^{-4}M$, solids concentration 2.5 g/l, pH = 3.5. Activation energy for the initial step is essentially zero; for the slow step, the temperature dependence of the first-order rate constant corresponds to an activation energy of 2.4 kcal/mole

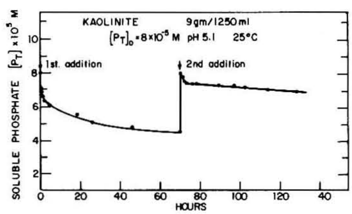

Figure 6. Effect of successive additions of phosphate to alumina and kaolinite over relatively short time intervals

Note that the capacity for phosphate removal decreases with each addition a first-order rate constant (range 1 to 22 days) of 0.01–0.05 day^{-1}. These values, though imprecise, are of the same order of magnitude as our observed value of 0.024 day^{-1} at pH 3.5 on α-Al_2O_3 (see Table I). Their rates in the first few hours were more than 100 times greater. Burns and Salomon (1969) studied the rapid adsorption of phosphorus from seawater on kaolinite, but since their experiments were carried out at high pH (7.0) and terminated after 50 hr, they did not observe the slow reaction step.

This study, while by no means resolving all the notational confusion nor all the conflicting theories and observations in the literature, provides the following new information: the slow reaction is apparently first-order in phosphate over the period from 1–60 days; the temperature influence is primarily on the slow following step and not on the rapid initial step; addition of fluoride as a typical complexing agent (Figure 1) decreases the amount adsorbed in the initial step but not the rate constant for the slow step; and successive addition of phosphate on a short time scale (Figure 6) results in a decreased capacity for phosphate removal, but on a long time scale (Figure 7) the total amount removed and its rate of removal are the same for the second addition as for the first.

In a previous paper (Chen et al., 1973), we discussed in detail the rapid adsorption step at 25°C and the influence of additives on the amount adsorbed, so that these results will not be repeated here. The mechanism of adsorption is complex and depends on the pH range under consideration.

The mechanism of phosphate removal in the slow following step almost certainly involves the growth of new aluminum phosphate phases (Kittrick and Jackson, 1954; Hemwall, 1957a,b). There has been considerable confusion over the mechanism, however. Certainly, this process involves the release of aluminum ions from the lattice of alumina or kaolinite (Low and Black, 1947; Bache, 1964; Hemwall, 1957b; Hsu and Rennie, 1962), the diffusion of phosphate from solution to react with these ions, the nucleation of a new crystal phase, and the growth of these crystals. Within the ranges of parameters studied, we have eliminated as a rate-determining step either diffusion (Kar, 1958) or release of aluminum ions from the lattice (Gaines and Rutkowski, 1957). If either of these steps were rate-determining, the rate law would not show the observed linear dependence of rate on phosphate concentration. Thus, we hypothesize that nucleation and growth of a new phase are the rate-determining steps under our experimental conditions.

The nature of the phase or phases formed is still open to question. We have verified that at high concentrations of phosphate an $AlPO_4$ material similar to variscite is formed (Table III), but only the crystal morphology (hexagonal plates, as in Figure 3) leads us to infer that the same crystal phase is formed at low concentrations. Other studies have identified phases similar to taranakite or Minyulite (Kittrick and Jackson, 1956) or palmerite (Haseman et al., 1950) in the products of phosphate reaction with clay minerals. Palmerite, in particular, is described as forming "distinct hexagonal-shaped crystals" (Haseman et al., 1950).

Our experiment in which crystalline variscite was added (Figure 8) and caused a *decrease* in reaction rate instead of the expected increase, only confirms the notion that the growth of this new phase is more complicated than a simple stoichiometric reaction to form $AlPO_4 \cdot nH_2O$.

Nevertheless, the new phase does seem to have some of the attributes of an aluminum phosphate. For example, the rate of the slow step decreases with increasing pH, going essentially to zero at pH ≥7, in just the region where one expects to see incongruent dissolution of $AlPO_4$ to give $Al(OH)_3$ and soluble phosphate. Of course, the free energies of the substances involved in these reactions are poorly known and in any case depend strongly on age and crystal morphology (Chen et al., 1973) but it is not surprising that when the free energy of formation of $AlPO_4$ tends to zero, so does the rate of the slow reaction of phosphate uptake by aluminum oxide and kaolinite.

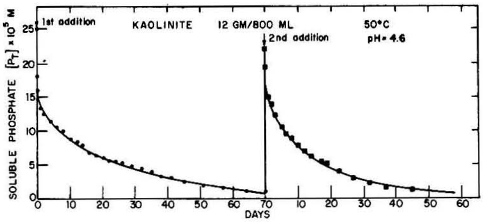

Figure 7. Effect of successive additions over long periods of time of phosphate to kaolinite

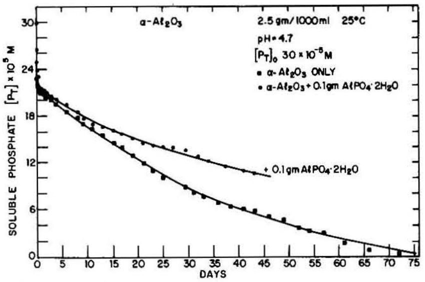

Figure 8. Effect of a seeding with meta-variscite ($AlPO_4 \cdot 2H_2O$) is to *decrease* the rate of phosphate removal by alumina. This is the opposite effect from that predicted by the hypothesis that the new phase formed is a meta-variscite

Our analyses of the supernatant solution for aluminum also bear this out. In Table II, a simple chemical model (Sillen and Martell, 1964, 1971) Al^{3+}, $AlOH^{2+}$, $Al(OH)_4^-$, and the various protonated ortho-phosphates (but no polymeric Al species) were used to calculate the solubility product K_{so} of a hypothetical precipitate of $AlPO_4$. The values of pK_{so} obtained in the pH range from 3.5–6.2 were essentially constant and independent of whether the substrate was alumina or kaolinite. The average (pK_{so} = 19.9 ± 0.5) is close to values previously reported for "amorphous $AlPO_4$" (Cole and Jackson, 1950; Taylor and Gurney, 1962) but not so small as the values for crystalline variscite: pK_{so} = 21.0 (Kittrick and Jackson, 1955) pK_{so} = 22.0 (Bache, 1963) or pK_{so} = 22.5 (Taylor and Gurney, 1964).

At higher pH values, the concentration of aluminum in solution is close to what one might expect from the equilibrium solubility of amorphous $Al(OH)_3$ and higher than Gibbsite. Apparently there was a trace of phosphate in the initial solutions even before the known addition of phosphate was made (Chen, 1972) since the aluminum concentrations measured at low pH before phosphate addition are very close to those measured after one week digestion in the presence of phosphate, and very much lower than the calculated equilibrium concentration for aluminum hydroxide. These aluminum concentrations were similar to those observed in clays and soils (Lindsay et al., 1959; Raupach, 1960). The constancy of aluminum concentration in solutions resulting from phosphate reaction with aluminum oxides or clay minerals has been noted before many times (Hsu and Rennie, 1962; Hemwall, 1957b; Bache, 1964).

Nucleation and growth are favored as rate-determining by the above evidence and probably also by the increased reaction rate with increased surface area (Table I and Figure 4), as well as the relatively small effect of temperature (Figure 5). The fact that successive additions of phosphate result in essentially the same first-order rate constant for the slow step (even though the reactive sites for the fast step have been used up) also points to this mechanism.

The principal alternative mechanism, where lattice dissolution to give soluble Al species is rate controlling, would certainly predict an increased reaction rate with increasing surface area, would probably predict a larger increase in rate with increasing temperature, as well as the decrease in rate at increased pH. However, this mechanism would be unlikely to account for rigorous obedience to a first-order rate law over long periods of time, and would be more likely to predict a rate which was zero-order in phosphate. This latter effect was definitely not observed.

To put these results in the context of phosphate removal by sediments in natural waters, it is helpful to summarize the reaction rate law for the slow step in the following form

$$-\frac{d(\mathrm{P})}{dt} = kAS(\mathrm{P})$$

where (P) is the total concentration of orthophosphate species, A is the specific surface area of the sediment (m^2/g), S is the concentration of sediment (g/l), and t is time in days. The value of the rate constant, k, at $pH = 5$ is of the order of 2×10^{-4} for kaolinite and 8×10^{-4} for α-Al_2O_3, using the data of Table I and assuming that these proportionalities hold over a wider range than our limited data. As pH is increased to 7.0, these constants decrease by more than a factor of 10. Except for pH, the most complicated effects of changes in sediment or water composition will probably be on the initial rapid adsorption step, but the slower step may account in many cases for the majority of phosphate removed over periods of a month or more, particularly from interstitial waters of clay-based sediments.

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Removal of Chromate from Cooling Tower Blowdown by Reaction with Electrochemically Generated Ferrous Hydroxide

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■ Treatment of cooling tower blowdown with electrochemically generated $Fe(OH)_2$ quantitatively reduced Cr(VI) to Cr(III) and concurrently precipitated it without pH adjustment. Concentrations of Cr(VI) of <0.005 mg/l. were achieved. $Fe(OH)_2$ treatment also precipitated a large fraction of the phosphate and other anions to improve product effluent quality significantly with respect to total dissolved solids. Steady-state generation of $Fe(OH)_2$ in blowdown was accomplished with high Faraday efficiency in a flow cell which utilized sacrificial low-carbon steel anodes and stainless steel cathodes. Colloids were formed under most electrolysis conditions, and special procedures were required to obtain filterable precipitates.

Chromate salts are used commercially for corrosion control in cooling water systems. Wastes from chrome plating baths contain both chromate salts and chromic acid. Removal of chromium from these waste effluents prior to return to natural waterways is a major environmental problem. Hexavalent chromium is especially undesirable since it is known to be carcinogenic (Amer. Pub. Health Assoc., 1965) and also deleterious to sewage plant operation (Siegerman, 1971).

Levels of chromium allowed in waste effluents which are returned to natural waterways and underground reservoirs by Federal law are presently controlled by state environmental improvement and protection agencies. The U.S. Public Health Service has specified a maximum Cr(VI) concentration of 0.05 mg/l. for drinking water.

Treatment for Cr(VI) removal usually involves chemical reduction to Cr(III) with SO_2, sulfite salts, $FeSO_4$ (Carls and Schieber, 1971), or $Na_2S_2O_5$ (Balden, 1959) all at pH 2.5 to 3. Cr(III) is then precipitated at pH 8.5 by adding NaOH or CaO. These procedures increase total dissolved solids (Na_2SO_4 or $CaSO_4$) in the treatment process by an estimated 200 mg/l. for a Cr(VI) content of 15 mg/l.

Several other methods of treatment which have been reported include reduction by scrap iron (*Air, Water News,* 1971), iron chips (Selm and Hulse, 1962), iron powder (Hine, 1969), metal sulfides (Lancy, 1966), electrochemical reduction with carbon particles (*Products Finishing,* 1970), and ion exchange (Carls and Schieber, 1971).

A new method of treating cooling tower blowdown utilizing electrochemically generated $Fe(OH)_2$ as the reducing agent is reported here. Cr(VI) is reduced quantitatively to Cr(III) by $Fe(OH)_2$ and concurrently precipitated without adjusting the pH of the blowdown before or after electrolysis. The reaction can be written:

$$0.5Cr_2O_7^{2-} + 3Fe(OH)_2 + 3.5H_2O \rightleftharpoons Cr(OH)_3 + 3Fe(OH)_3 + OH^- \quad (1)$$

The free energy change, $\Delta G°$, for this reaction in neutral solution was computed from Latimer's data (1952) to be −38.3 kcal/mol of Cr, and it is almost as large as for the reaction in acid solution:

$$HCrO_4^- + 7H^+ + 3Fe^{2+} \rightleftharpoons Cr^{3+} + 3Fe^{3+} + 4H_2O \quad (2)$$

where $\Delta G°$ is −40.1 kcal/mole of Cr.

In this paper are reported the results of laboratory batch and flow cell experiments which were done to test improvement of water quality with respect to Cr(VI), Cr(III), soluble orthophosphate, soluble condensed phosphates, and total dissolved solids.

Experimental

The source of waste water was cooling tower blowdown effluent from the Los Alamos Scientific Laboratory power plant. The cooling water is routinely made up from secondary sewage effluent from the Laboratory Technical Area treatment plant, and a proprietary corrosion inhibitor (Betz Laboratories, Trevose, Pa.) containing chromate, phosphate, and zinc is added. Typically, the quality of the secondary sewage effluent is very good: chemical oxygen demand, 25 mg/l.; total dissolved solids, 210 mg/l.; total soluble phosphate (soluble orthophosphate plus soluble condensed phosphates which hydrolyze to orthophosphate), 2 mg/l. P. The cooling water is recirculated as many as four times and total dissolved solids in the blowdown increases by a factor of three or four.

Cr(VI), total Cr, soluble orthophosphate, and soluble condensed phosphate analyses were done, usually in triplicate, according to Standard Methods (Amer. Pub. Health Assoc., 1965). The permanganate method was used for total Cr, and the stannous chloride modification was used for phosphates.

Total dissolved solids were analyzed at 103°C by a procedure developed in this laboratory to obviate the need for desiccation of samples. Analyses were done in an air conditioned laboratory at 22.5 ± 1°C and about 50% relative humidity. Clean 250-ml beakers were dried for several hours at 103°C, cooled in air for 20 min, then tared to the nearest 0.1 mg. A top-loading Mettler balance was used to weigh 200 ± 0.05 grams of liquid sample which had been passed through a 0.45-μ membrane (Millipore) filter. After evaporation of samples to dryness on a steam plate, they were heated for at least 24 hr at 103°C, then weighed to the nearest 0.1 mg after cooling in air for 20 min. By this procedure, moisture absorption by samples after heating at 103°C was minimal, and not significantly different than if samples were desiccated prior to weighing. Triplicate samples were reproducible to a precision generally better than 3%. Beakers were conveniently cleaned for reuse with 1*M* oxalic acid and a brush to remove adherent solids.

Batch electrolyses were done with 1.8 l. of waste water in a 2-l. beaker. The cathode was a 316 stainless steel sheet 9.4 × 17 × 0.08 cm, positioned parallel to a mild cold-rolled steel (AISI C1010) anode of similar dimensions and separated at top and bottom with nonconducting spacers

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approximately 2 mm thick. Effective area of each electrode was 140 cm². The electrolyte was stirred with a 3.5-cm Teflon-covered magnetic bar at about 2000 rpm, such that a vortex funnel extended about two thirds of the way down from the surface, and the electrolyte was continuously swirled between the electrodes, which were located close to the wall of the beaker. Before each electrolysis, the anode was cleaned with 1*M* oxalic acid, washed with distilled water, and then air dried for about 15 min prior to weighing and immediate use. Experiments were done at constant current, manually controlled, usually at 1 A. The voltage required for 1 A was in the range of 3–6. At the start of each experiment, a reverse polarity electrolysis was done for 15–30 sec. After electrolysis, the anode was quickly wiped and washed clean of adhering material with distilled water, then air dried for a few minutes before weighing.

Most of the precipitate was removed by rough filtering with a compressed plug of fiber glass wool in a polyethylene funnel. Suspended solids and colloid not removed by this procedure were removed with a 0.45-μ membrane (Millipore) filter prior to analyses for chromium, phosphate, and total dissolved solids.

Steady-state flow experiments were done by pumping the blowdown from a barrel through a calibrated flowmeter to the electrolysis cell described below, using a small centrifugal pump. Flow rates were controlled with a 5-mm bore glass stopcock.

The cell was fabricated with two removable 12.7 × 52.3 × 0.64-cm type AISI C1019 cold formed steel anodes placed between three 12.7 × 52.3 × 0.08-cm Type 316 stainless steel cathodes in an upright position and spaced 0.16 cm. Acrylic plastic was used to frame the electrodes in a rectangular box. Feed to the cell was from the bottom; the product effluent overflowed the electrodes at the top of the cell. Total effective area of the anodes was 2080 cm², since both sides of each were utilized. Both sides of the middle cathode and one side of each outer cathode were utilized. Anodes were cleaned with 1*M* oxalic acid shortly before use, and were also operated cathodically for about 30 sec immediately prior to making a run.

Results and Discussion

Results from batch (beaker) experiments did not appear to be significantly different from results from steady-state flow cell experiments. Consequently, the results are reported in terms of appropriate parameters rather than by type of experiments.

Anodization of Fe. $Fe(OH)_2$ is generated electrochemically according to the electrode reactions:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{anode} \qquad (3)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{cathode} \qquad (4)$$

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \qquad (5)$$

Faraday efficiencies for this process in the blowdown effluents were evidently close to 100% as shown by weight loss measurements in Figure 1 for batch experiments. Good weight-loss data for the flow cell were not obtained because of the inability of weighing the anodes precisely after each individual run. However, the accumulated weight loss for several runs was very close to that expected for 100% Faraday efficiency.

Other investigators have reported on the efficiency of Fe anodization in waste waters. Miller and Knipe (1965) reported that steel anodes were anodized with 91% efficiency in sewage effluents, and Sadek (1970) measured about 100% efficiency for synthetic sewage. Recent work in this laboratory showed near 100% efficiency for low carbon steel anodes in secondary sewage effluents in beaker experiments, but in flow cell experiments only 84% efficiency was measured.

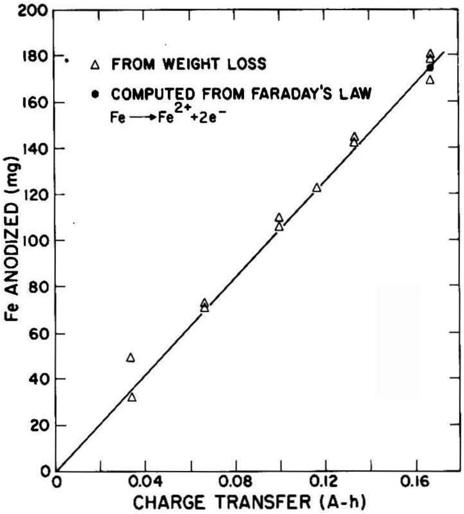

Figure 1. Faraday efficiency plot for $Fe(OH)_2$ generation in blowdown in batch experiments

Equation 3 is symbolic of the anode reaction, but probably it is not accurate for depicting the actual mechanism. Recent work by Bockris and co-workers (1971) on anodization of high purity Fe in neutral borate solutions showed that $Fe(OH)_2$ is formed as a layer on the anode. Similar behavior would be expected with blowdown, and under steady-state conditions the $Fe(OH)_2$ formed should be continuously ejected from the anode and react with Cr(VI) in solution.

Formation of Colloid. Colloids were formed in most of the electrolysis experiments. As a general rule, flocculated precipitates were obtained only when the amount of Fe anodized was <25 mg/l. or >200 mg/l. This behavior is in conformance with known coagulation phenomena (Stumm and O'Melia, 1968). For the former case, the precipitate was a mixture of Cr(III) and Fe(III) hydroxides and phosphates. For the latter case, the precipitate contained a large fraction of $Fe(OH)_2$ in addition to Cr(III) and Fe(III) hydroxides and phosphates.

As a practical matter, procedures were developed for obtaining filterable flocs while achieving quantitative Cr(VI) removal to concentrations of <0.005 mg/l. This could be done by three different procedures:

1. Electrolyze blowdown to give a concentration of Fe >200 mg/l.
2. Electrolyze blowdown to give a concentration of Fe >200 mg/l., then mix with unreacted blowdown to give the final product.
3. Electrolyze blowdown to give a concentration of Fe >200 mg/l.; electrolyze a second batch to give a concentration of Fe of 20–25 mg/l.; mix the two batches to give the final product.

Procedure 2 or 3 would ordinarily be preferred to minimize both iron consumption and electricity consumption, since 85 mg/l. of Fe would suffice. However, as will be seen later, for this stage of development, neither procedure 2 or 3 was effective for reducing total Cr to a very low level of <0.01 mg/l.

Removal of CR(VI) by $Fe(OH)_2$. Electrolytic reduction of Cr(VI) in blowdown on a stainless steel cathode could possibly occur (Uhlig, 1962), but evidently the rate is very low, since exploratory electrolyses with a stainless steel anode (which was passive) and stainless steel cathode showed essentially no reduction of Cr(VI).

Removal of Cr(VI) by batch electrolysis with a Fe anode is demonstrated in Figure 2. Reduction to Cr(III) was very efficient until the concentration of Cr(VI) became small. The amount of Fe(II) required for quantitative removal of Cr(VI) was about 65 mg/l. as shown in Table I. (Note that total Cr removal is covered in a later section of this discussion.)

Partial reduction of Cr(VI) in the flow cell was also very efficient as shown by Table II.

However, when a mixing procedure was used to obtain a filterable floc, the amount of Fe(II) required for complete Cr(VI) reduction was greater than with a batch electrolysis. Table III shows this effect. About 85 mg/l. of Fe(II) was required.

These results indicate that flocculated $Fe(OH)_2$ is not as effective as freshly generated $Fe(OH)_2$ for removal of last traces of Cr(VI) to a concentration of <0.005 mg/l.

Some experiments also were done by a mixing procedure where untreated blowdown was mixed with electrolyzed blowdown containing flocculated $Fe(OH)_2$. The amount of Fe generated was >200 mg/l., and the amount of Fe added to the product after mixing was about 100 mg/l. Product effluents obtained under these conditions invariably contained <0.005 mg/l. of Cr(VI).

The competing reaction of oxidation of $Fe(OH)_2$ by dissolved oxygen probably accounts for the decreased efficiency of reduction of Cr(VI) to Cr(III) at low concentrations. With a dissolved O_2 concentration of 6.5 mg/l. in the blowdown, the amount of Fe(II) consumed by the reaction:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightleftarrows 4Fe(OH)_3 \qquad (6)$$

would be 45 mg/l. Although this reaction has a $\Delta G°$ of -22.1 kcal/mol of Fe, it is slower and secondary to reaction 1 where $\Delta G°$ is -12.8 kcal/mol of Fe (Latimer, 1952).

Removal of Cr(III). Data were obtained on soluble Cr(III) remaining in electrolyzed blowdown and the resulting product effluents (Table IV). Determinations are reported only for products in which Cr(VI) was present in concentrations of <0.005 mg/l. and filterable flocs were obtained. Untreated blowdown pH values were in the

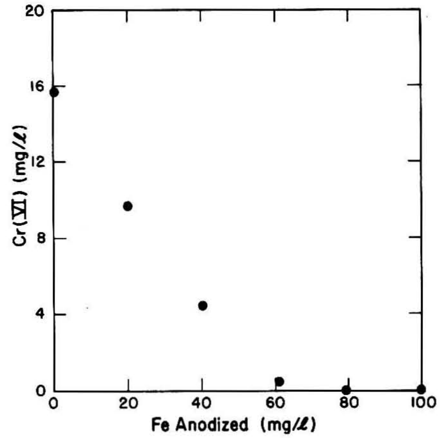

Figure 2. Removal of Cr(VI) by beaker electrolysis at 1 A. Fe was anodized at a rate of 17.4 mg/min

Table 1. Removal of Cr(VI) by Batch Electrolysis at 1 Ampere

Elect. time, min.	Fe anodized, mg/l.	Starting Cr(VI), mg/l.	Product Cr(VI), mg/l.	Cr(VI) Removal, %	Efficiency of removal, %[a]
6.0	58	13.77	1.42	89.7	79
6.0	61	15.59	0.37	97.6	84
7.0	68	15.48	<0.005	>99.96	75
8.0	79	13.77	<0.005	>99.96	57
8.0	79	15.59	<0.005	>99.96	65
10.0	101	15.48	<0.005	>99.96	50

[a] Computed on the basis of 3 moles of Fe(II) per mole of Cr(VI).

Table II. Partial Reduction of Cr(VI) in Flow Cell at 2.5 Amperes

Flow rate, l./min	Fe anodized, mg/l.[a]	Starting Cr(VI), mg/l.	Cr(VI) removal, %	Efficiency of removal, %
1.50	22.2	13.28	45.7	99.9
1.50	22.2	14.28	45.7	96.4
1.50	22.2	13.10	50.6	98.1
1.50	22.2	13.45	54.3	100.0
1.95	28.9	14.13	59.1	93.7
1.95	28.9	12.96	62.7	92.4

[a] Computed from Faraday's law for 2-electron oxidation.

Table III. Removal of Cr(Vi) by a Mixing Procedure[a]

Volume mixing ratio	Fe added, mg/l.	Starting Cr(VI), mg/l.	Product Cr(VI), mg/l.	Cr(VI)removal, %	Efficiency of removal, %
4.39	60	13.45	0.62	95.4	74
4.39	60	13.10	0.21	98.4	72
3.51	79	14.28	0.053	99.6	59
3.10	84	15.48	0.006	99.96	61
2.33	106	13.28	<0.005	>99.96	41

[a] One batch was electrolyzed 2.5 A and 1.95 l./min to give Fe content of 22 mg/l., then mixed with second batch which was electrolyzed at 24 A and 1.50 l./min to give Fe content of 278 mg/l.

Table IV. Concentrations of Cr(III) in Electrolyzed Blowdown and in Product Effluent after Mixing

Electrolyzed blowdown		Product effluent	
Fe anodized mg/l.	Cr(III), mg/l.	Fe added, mg/l.	Cr(III), mg/l.
278	0.005	103	0.035
278	<0.005	106	0.017
231	<0.005	110	0.038
278	<0.005	132	0.021
278	<0.005	139	0.123
303	0.013	152	0.107

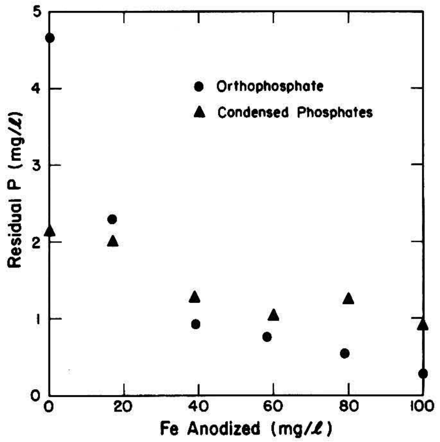

Figure 3. Removal of phosphates by beaker electrolysis at 1 A

range of 6.0–6.6 and product pH values were in the range of 6.8–7.8.

The concentrations of Cr(III) were low when large amounts of Fe were anodized in the blowdown, but the product effluents from mixing contained considerably more Cr(III). Adjustment of pH either before or after electrolysis possibly would improve Cr(III) removal.

Removal of Phosphates. Measurements were made on removal of soluble orthophosphate and soluble condensed phosphates. Figure 3 shows removal of phosphates from blowdown in a typical batch electrolysis. Figure 4 shows orthophosphate removal with respect to Fe anodized, and Figure 5 is a similar plot for condensed phosphate removal. Condensed phosphates were removed less efficiently than orthophosphate.

Residual orthophosphate concentrations after electrolysis (Figure 3) were similar to those measured by Recht and Ghassemi (1970) under comparable conditions by chemical precipitation with Fe(III) salts. For example, at pH 7.1 with a 2:1 Fe:P ratio, the residual orthophosphate concentration measured by Recht and Ghassemi (1970) was 1.8 mg/l. P, compared to the value of 2.3 mg/l. in Figure 3 for the same 2:1 Fe:P ratio. The residual orthophosphate concentration apparently is determined primarily by solubility limitations of Fe(III) orthophosphate.

Reduction in Total Dissolved Solids (TDS). Product effluents were definitely improved with respect to TDS. Data for flow cell runs are shown in Figure 6 with percentage reduction in TDS plotted as a function of Fe anodized. Substantial reductions averaging 22% were obtained for about 100 mg/l. of Fe, and larger reductions averaging 40% were measured for 280 mg/l. of Fe. A surplus of electrochemically generated precipitate is significantly beneficial for product effluent quality with respect to TDS.

Reagent and Energy Costs. Removal of Cr(VI) to a concentration of <0.01 mg/l. would require about 0.8 lb of

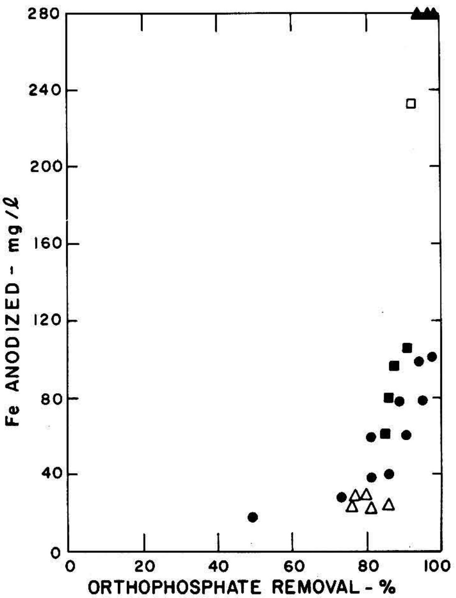

Figure 4. Removal of orthophosphate by electrolysis. Mean concentration in untreated blowdown was 5.67 mg/l. P

● 1-A beaker electrolysis product, △ 2.5-A flow cell electrolysis product, □ 20-A flow cell electrolysis product, ▲ 24-A flow cell electrolysis product, ■ 24-A flow cell electrolysis product mixed with 2.5-A flow cell electrolysis product

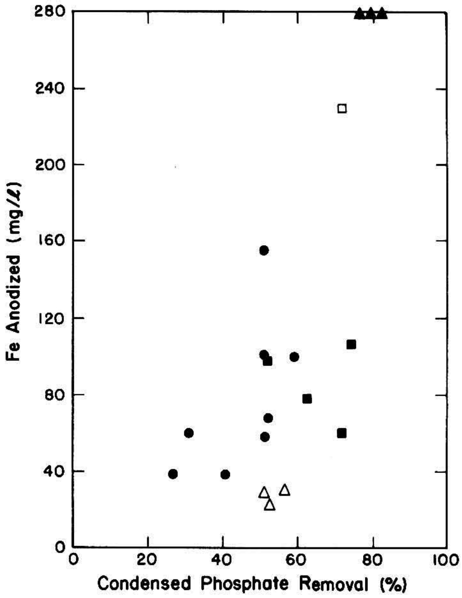

Figure 5. Removal of condensed phosphates by electrolysis. Mean value in untreated blowdown was 2.64 mg/l. P

● 1-A beaker electrolysis product, △ 2.5-A flow cell electrolysis product, □ 20-A flow cell electrolysis product, ▲ 24-A flow cell electrolysis product, ■ 24-A flow cell electrolysis product mixed with 2.5-A flow cell electrolysis product

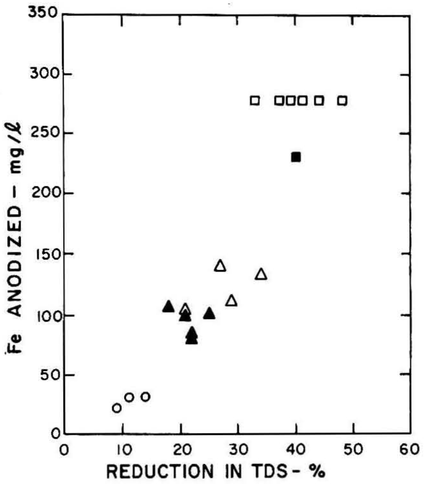

Figure 6. Reduction in total dissolved solids for blowdown feeds initially containing 720 to 990 mg/l. TDS

○ 2.5-A electrolysis product, □ 24-A electrolysis product, ■ 20-A electrolysis product, △ 24-A electrolysis product mixed with untreated blowdown, ▲ 24-A electrolysis product mixed with 2.5-A electrolysis product

low carbon steel per 1000 gal of product effluent. At a cost of 12 cents per lb, the Fe reagent cost would be about 10 cents per 1000 gal of product effluent, exclusive of shipping and handling costs.

Approximately 2 kwh (dc) per 1000 gal of product effluent would be required for a driving potential of 5 V.

Significance of Results

Recently many users of the proved chromate corrosion-prevention method have chosen to abandon it rather than go to the expense of special waste-treatment facilities. In the long run, this may not be an economically desirable course, because the substitute materials may prove more expensive than the continued use of Cr(VI) products coupled with effluent cleanup facilities. Furthermore, many users of Cr(VI) chemicals such as electroplaters have no alternative but to install effluent treatment facilities.

The electrochemical ferrous hydroxide precipitation process is worthy of further study and development because it offers a means of effectively removing total chromium while, at the same time, reducing phosphate by 80% or more and reducing TDS by up to 40%.

Primary advantages of the method are: Reduction and precipitation are done concurrently without adjustment of pH. Extraneous soluble ions are not added to increase TDS and also increase reagent cost. (There is a beneficial decrease in TDS by co-precipitation of Fe and Cr compounds in the flocs.) Reagent is added accurately and simply by controlling feed flows and current flows, and can be done in the steady-state mode for automated operation.

Disadvantages of the method are: Stable colloids are formed under most conditions which usually are optimum for quantitative Cr(VI) removal. Excessive amounts of anodized Fe are required for quantitative Cr(III) precipitation (<0.01 mg/l), and for maximum improvement in TDS. Direct current power is required.

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Tracing Atmospheric Pollutants by Gas Chromatographic Determination of Sulfur Hexafluoride

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■ Based on a nitric oxide treated molecular sieve column which quantitatively elutes SF_6 prior to the components of air, laboratory and portable electron capture gas chromatographic procedures have been developed to determine SF_6 down to a sensitivity of less than 4×10^{-13} cm^3/cm^3 without preconcentration. The laboratory chromatograph can measure the SF_6 concentration in collected air samples at a rate of 1 every 5 min. Application to plume studies by simultaneous determination of SO_2, sulfate, and SF_6 showed that the measured decrease of pollutant concentration was primarily attributable to dilution. The portable real-time instrument, which has been used in aircraft and land vehicles, can continuously measure the SF_6 tracer gas down to a sensitivity of 4×10^{-13} cm^3/cm^3 for a duration of 40–60 sec with a response time of about 3 sec for a tenfold concentration change. The capability of airborne power plant plume crosswind concentration gradient determinations using SF_6 is demonstrated. Tracing air masses for 100 or more kilometers during unstable meteorological conditions appears feasible.

Monitoring of our environment is becoming increasingly important both to the concerned public and to pollution control researchers. Numerous instruments and methods are available for measuring gaseous and particulate pollutant concentrations (Hochheiser et al., 1971) in the atmosphere but tracing and determining the source of these pollutants, especially at distances greater than 15 km, have not been as extensively and successfully studied. Sulfur hexafluoride has proved to be a useful tracer for such dispersion studies because of its ultrasensitive detection by electron capture chromatography, chemical stability in the presence of other atmospheric pollutants and sunlight (Saltzman et al., 1966), and normally low concentration in the atmosphere—less than 2 parts in 10^{13} by volume (Lovelock, 1971). Early chromatographic methods of analysis employed alumina or silica gel and charcoal columns in series (Clemons et al., 1968; Turk et al., 1968; Hawkins et al., 1971), but the SF_6 peak always eluted on the tail of the large oxygen peak preventing the determination of low concentrations of SF_6 ($<10^{-11}$ cm^3/cm^3) without preconcentration.

Concurrently with Simmonds et al. (1972), an improved laboratory electron capture gas chromatograph method for the direct determination of collected air samples containing as little as a few parts of SF_6 in 10^{13} parts of air has been developed (Dietz and Cote, 1971); the technique and its application to plume tracing and chemistry studies are described in this paper. Additionally, a portable gas chromatograph, which has been developed for real-time determination of SF_6 in meteorological tracer studies using aircraft and land vehicles (Dietz et al., 1972), is also described including examples of the determination of SF_6 concentration gradients in power plant plume crosswind measurements. The application to plume chemistry studies for determining chemical conversion by measuring changes in the pollutant-to-SF_6 concentration ratio is also indicated.

Experimental

Laboratory Chromatograph. The laboratory instrument used in these determinations was a Varian Aerograph Model 1532-2B with a concentric tube type 250-mCi tritium foil electron capture detector. The 1-mV recorder was equipped with a Disc Integrator and a low pass noise filter consisting of two 3000-ohm resistors and a 100-μf capacitor at the input terminals. The filter reduced the amplified detector noise by about a factor of five without affecting the SF_6 signal. Ultrapure N_2 from Baker or Matheson was satisfactory as the carrier gas after passing through an anhydrone dryer; the use of a BTS catalyst gas purification train (Maak and Sellars, 1965) did not produce any significant improvement in detector sensitivity. The 17-ft by ⅛-in. gc column (all tubing was stainless steel) and the 3-ft by ⅛-in. precut column contained Molecular Sieve 5A treated with nitric oxide (Dietz, 1968) to reduce tailing of the SF_6 peak; following treatment the columns were purged with carrier gas overnight at 325°C.

The purpose of the precut column was to prevent components of the atmospheric sample other than SF_6 from reaching the detector. Optimum sensitivity was achieved with the detector at 100°C and 65 V dc at a carrier gas flow rate of 14 cm^3/min. When accumulated contaminants began to affect the detector standing current (about 4–6 weeks), the column was cleaned by heating overnight at 300°C with the carrier gas flowing. The precut column was normally outgassed at the same temperature every two or three days. Details of the plumbing configuration are presented elsewhere (Dietz and Cote, 1971).

Portable Chromatograph. The portable gas chromatograph used in this study was an Anayltical Instrument Development Model 510 equipped with a 200-mCi tritium foil parallel plate type electron capture detector designed to operate under pulsed mode with 5% methane in argon as carrier gas. The only major modifications to the original instrument consisted of replacement of the Teflon cylinder within the detector with one of glass since Teflon absorbs SF_6, removal of the needle injection port, and conversion of the detector to dc operation by installing an adjustable potentiometer on an internally available +15 V dc terminal. The chromatograph contained its own rechargeable batteries for electrometer and detector operation (sufficient for >10 hr). Additionally, 350 W at 120 V ac was required for operation of a modified Varian 7-port solenoid-operated sampling value, a Honeywell Model 19 recorder, and a positive-displacement sampling valve.

The mode of operation of this real-time instrument was frontal chromatography since a column short enough to elute the SF_6 in real-time (2–4 sec) by conventional chromatography was too short to effect a separation of the SF_6 from the air of the sample. During sampling, the argon backflush gas in the column was displaced with the air being analyzed with the recorder output in the form of a step (frontal) in place of the usual SF_6 peak. A constant height for the SF_6 frontal was indicative of a constant concentration in the air being sampled; when the SF_6 concentration varied, as when crosswind traversing a plume spiked with SF_6, the SF_6 frontal height also varied in a similar fashion.

A schematic diagram of the flow system and sampling

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valve is shown in Figure 1. In the backflush position pure argon was sent to the detector (ports 4-5) while the column (6-ft by ⅛-in. packed with Molecular Sieve 5A, 60–80 mesh) was backflushed with argon (ports 7-6, 2-3). Port 3 was connected to the upstream side of the back-pressure regulator so that the column could be brought to sampling pressure prior to switching. The argon was regulated to 20 psig (gauge 2) producing a 70 to 80 cm^3/min backflush and the needle valve was adjusted for a detector purge of 40 cm^3/min; the detector voltage was approximately 7 V dc. The molecular sieve column was treated with nitric oxide as previously described as was the 3-in. by ⅛-in. molecular sieve dryer ahead of the detector. This latter short column was necessary to produce a stable baseline since trace impurities from the sampling valve (lubricant vapors, etc.) would have otherwise adversely affected the detector.

About 20 sec before sampling, the air-sampling pump was activated and the back-pressure regulator was set to 11 psig (gauge 1) to purge the pump and sampling valve between ports 1b and 1a (the latter was an added modification to the original valve). After energizing the solenoid switching valve, approximately 20 cm^3/min of the air to be analyzed was passed through the column (ports 1b-2). Both the columns and the detector were at 25°C. About 39 sec after sampling commenced, the SF_6 frontal reached the detector followed by the O_2 frontal 46 sec later. This gave an effective continuous determination of SF_6 for a duration of three quarters of a minute—sufficient, for example, to traverse a plume crosswind section. At this point, the solenoid switching valve was de-energized to backflush the remaining components of the atmospheric sample through the main vent (the air-sampling pump was turned off and the back-pressure regulator was reduced to 0 psig). Depending on the concentration range of the SF_6, the column was backflushed for 1–4 min before the next sampling commenced in order to remove the O_2 from the previous sample.

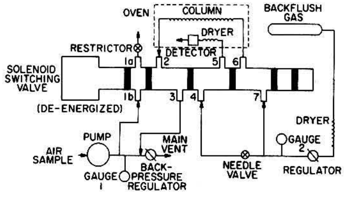
Both the laboratory and real-time portable chromatographs were calibrated with gas mixtures ranging from 2×10^{-12} to 10^{-9} part of SF_6 per part of air. The gas mixtures were precisely prepared by pressure-dilution measurements from a working standard of 85 ppm SF_6 in N_2 mixture prepared by the same technique. This latter mixture was checked for accuracy using an F&M Model 810 chromatograph (Hewlett-Packard) with a thermal conductivity detector and molecular sieve column (Dietz, 1968) calibrated with pure SF_6.

Atmospheric Sampling Cannisters. For determination of SF_6 with the laboratory instrument, 900-cm^3 steel bottles, each equipped with a toggle valve, critical orifice, filter, and quick-connect fitting, were used in an aircraft to obtain samples from power plant plumes as described elsewhere (Manowitz and Tucker, 1969). Analyses were performed on a routine basis by either pressurizing the collection bottles to about 2 atm absolute with ultrapure N_2, allowing ample time for mixing, and expanding through the chromatograph sample loop or by evacuating the sample loop up to the collection bottle and allowing the undiluted sample to expand into the loop. When suitable pressure corrections were applied, the results agreed within 3% by either method.

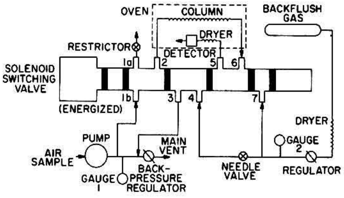
Results

Calibration. The concentration of the SF_6 working standard as determined by the TC chromatograph was 85 ± 2 ppm—in excellent agreement with that calculated from the pressure-dilution measurements of 84 ± 1 ppm. When the SF_6 in air mixtures prepared from the working standard was used, the calibration curves for both electron capture chromatographs were nearly linear up to 10^{-9} cm^3/cm^3 with a limit of detection at three times noise of about 4×10^{-13} cm^3/cm^3.

Laboratory Chromatograph. Backflushing the precut column at the appropriate time after sample injection prevented the major fraction of the oxygen from the air sample from reaching the gc column and detector, thus considerably shortening the time for a complete analysis. In the upper chromatogram of Figure 2, the precut column was backflushed 1.5 min after sample injection; this caused most of the oxygen of the laboratory air sample to be vented and allowed only a small amount (<100 ppm) to reach the detector. The lower chromatogram shows that by backflushing 55 sec after injection, all but a very small amount of oxygen (<10 ppm) was eliminated. The com-



BACKFLUSH POSITION



SAMPLING POSITION

Figure 1. Schematic of portable chromatograph piping configuration showing the solenoid switching valve in backflush and sampling positions

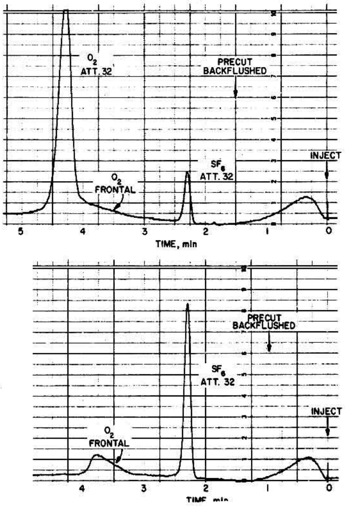


Figure 2. Chromatograms of room air samples

17-ft NO-treated Molecular Sieve 5A column at 100°C with a 2-cm^3 sample loop. Top: precut column backflushed at 1.5 min after sample injection (SF_6 measured concentration, 2×10^{-12} cm^3/cm^3). Bottom: backflushed after 55 sec (SF_6 concentration, 6.6×10^{-12} cm^3/cm^3)

plete SF_6 peak was eluted from the precut column in less than 30 sec and was, therefore, not affected by the 55-sec backflush. With this technique, collected air samples were analyzed every 5 min.

Plume Analyses. The use of SF_6 as a tracer gas in power plant plume studies is exemplified by the results shown in Table I for data obtained in the plume of the Long Island Lighting Co. power plant at Northport. Procedures for sampling and determining the sulfur dioxide and sulfate concentrations are described elsewhere (Manowitz and Tucker, 1969). To calculate the individual concentration ratios and their associated error limits, the following estimated errors were assumed for the measured concentrations: SF_6, ±5% of measured value; SO_2, ±5% of measured value or 0.005 ppm, whichever was greater; SO_4, ±5% of measured value or 0.7 ppb, whichever was greater.

From the SO_2-to-SF_6 ratio, it was observed that the conversion or loss of SO_2 could range anywhere from 0 to 40%. Based on the SO_4-to-SF_6 ratio, however, the conversion to sulfate, beyond 2 km downwind (2.5 min downwind), appeared to range from 4–8%. An evaluation of a larger number of plume experiments based on the sulfur isotope ratio tracer technique showed similar results (Manowitz et al., 1970). These results were also in agreement with those of other workers (Urone and Schroeder, 1969; Dennis et al., 1969).

Portable Chromatograph. The rapid response of the instrument to a change in concentration and the constant height of the SF_6 frontal for a constant concentration is shown by the chromatograms in Figure 3. There was little loss of resolution when switching between the two mixtures every 4 sec and the response time to an instantaneous order of magnitude change in SF_6 concentration was determined to be about 3 sec.

Airborne Real-Time Determinations. The first flight test of the portable chromatograph for the determination of the injected SF_6 tracer was performed on August 11, 1971, at the LILCO Northport power plant. There was some difficulty in locating the edge of the plume to determine when the instrument should have been switched to the sampling mode as exemplified in the chromatograms of Figure 4. In the left determination, since the recorder response increased rapidly at the point of initial SF_6 frontal elution, it was apparent that sampling began at some point within the plume structure. From the other trace, however, the location of the SF_6 profile indicated that the instrument began sampling approximately 19 sec before entering the plume. Notice that the boundary line of the plume was sharp and that a continuous analysis of the entire SF_6 crosswind concentration was clearly displayed.

Table I. Northport Power Plant Plume Determinations. SF_6 Release Rate = 80 scfh, Wind ≈10 m/sec, April 14, 1970

	Measured concentrations			Concentration ratios[a]	
Distance from stack, m	SF_6, ppb	SO_2, ppm	SO_4, ppb	SO_2/SF_6	SO_4/SF_6
Background	0.0005	0.01	3.5	. . .	. . .
Breech	1540	1636	7040	. . .	5 ± 2
800	5.7	9.9	168	1740 ± 170	29 ± 3
	8.3	10.7	393	1290 ± 120	47 ± 5
2400	0.29	0.34	18.9	1140 ± 130	53 ± 8
	0.26	0.30	20.5	1120 ± 130	66 ± 10
4800	0.18	0.22	12.9	1180 ± 150	52 ± 10
	0.09	0.13	13.8	1350 ± 190	115 ± 20
8000	0.025	0.043	5.1	1360 ± 460	70 ± 60
16000	0.028	0.046	4.0	1330 ± 430	40 ± 40

[a] Corrected for background concentrations.

Following the successful development and flight testing of the SF_6 sniffer, a series of runs was made on August 30, 1972, at the Keystone Station power plant operated by Pennelec at Indiana, Pa. On board the plane with the SF_6 portable chromatograph (in foreground of Figure 5) was an optical densitometer which measured the particle concentration down to the atmospheric background of about 0.03 to 0.045 mg/m^3 by looking at the 90° light scattering from particles in the 0.01- to 10-μ size. The purpose of using the two units was to obtain two independent but essentially simultaneous determinations of the plume structure for comparison and confirmation of the two methods and for demonstration of the pollutant-to-SF_6 concentration ratio technique.

An example of the type of SF_6 chromatograms obtained from these runs is shown in Figure 6. The unstable meteorological conditions were evident in the meandering and sharp concentration gradients shown by the recorder during the 46 sec of actual SF_6 measurement (from 41–87 sec). The chromatogram from Figure 6 as well as the optical densitometer data was converted, with the aid of a Hewlett-Packard computer-calculator and plotter system, to concentration vs. distance as shown in Figure 7. It can be seen that the SF_6 sniffer and the optical densitometer produced nearly identical traces, thus corroborating their individual performance. The computed average SF_6 concentration over the width of the plume (7000 ft) was 6.4×10^{-11} cm^3/cm^3 which was more than 100 times greater than background whereas that of the particles, 0.054 mg/m^3, was only 1.2 times the background particle concentration (0.045 mg/m^3).

Discussion

SF_6 Absorption on Teflon. The sampling canisters used to collect air samples for subsequent determination of SF_6 with the laboratory chromatograph contained a ¼-in. pipe fitting for connection to the critical orifice; pipe thread sealant of the Teflon tape variety was found to absorb SF_6 leading to subsequent errors.

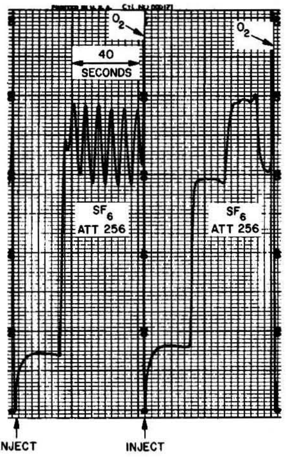


Figure 3. Frontal chromatograms showing the effect of cycling between two mixtures of SF_6 in air

6-ft NO-treated Molecular Sieve 5A column at room temperature. SF_6 concentrations: upper plateau, 5.0×10^{-10} cm^3/cm^3; lower, 3.0×10^{-10} cm^3/cm^3. Duration that each mixture was sampled alternately: left, 4 sec; right, 20 sec

As an example of this absorption effect, a typical bottle with Teflon tape on the pipe threads was filled to atmospheric pressure with 2 ppm SF_6 in N_2. After standing for several minutes, the bottle was evacuated for about 10 min and refilled with ultrapure N_2. The pumping and refilling were repeated for a total of 8 times after which a determination indicated an SF_6 concentration of less than 2×10^{-13} cm^3/cm^3. One week later the bottle was analyzed and found to contain an SF_6 concentration of about 1×10^{-11} cm^3/cm^3. A similar experiment repeated with polyethylene as the thread sealant gave an analysis for SF_6 of about 7×10^{-13} cm^3/cm^3. Thereafter the sampling canisters were used with polyethylene thread sealant.

A similar problem was encountered with a chromatograph gas sampling valve which contained a ceramic-filled Teflon cone seal; the valve exhibited the same absorption effects and gave poor results for SF_6 determinations below 10^{-11} cm^3/cm^3. The Varian tube-type sampling valve with Viton quad rings showed no such effect. For the same reasons, the cylindrical Teflon electrode spacer in the detector of the portable instrument was replaced with one of glass.

Calibration Gas Mixture. Daily checks were made of the calibration curves for both the laboratory and portable chromatographs using the prepared mixtures. At the 10^{-10} level, there was no detectable change in concentration over a period of 12 months when compared to freshly prepared mixtures. The 10^{-11} mixture appeared to decrease in concentration by about 1% per month for the same time period. One cylinder of air which was found to have contained 2×10^{-12} cm^3/cm^3 showed no change with time. Additionally, a number of halogenated hydrocarbons were sampled but none could be detected eluting before O_2 nor interfering in any way.

Applications to Tracer Studies. The errors associated with the independent collection of SF_6 and SO_2 in plumes followed by analysis later in the laboratory plus the need to make multiple passes to collect sufficient SO_2 limited the determination of individual SO_2 to SF_6 concentration ratios to a precision of ±15 to 30% (greatest at larger distances downwind). Chemical conversion of the SO_2 was determined to be only between 0 and 50% because of the large errors. In addition, both for plume studies and ground level measurements at great distances from the source (>15 km), there was no assurance that the gas-sampling canisters and hi-vol samplers were located in the correct places. Thus, large numbers of collection sites were needed and hours to days passed before the results were known.

The real-time portable chromatograph demonstrated that many of these disadvantages were significantly reduced. When used in conjunction with another real-time instrument, such as the optical densitometer for particle measurements, a much more accurate measurement of the pollutant-to-SF_6 concentration ratio was determined from the ratio of the total area under both curves. Based on the

Figure 4. Portable chromatograph in position on plane

Batteries and dc to ac inverters in right foreground; optical densitometer for particle concentration determination in left background

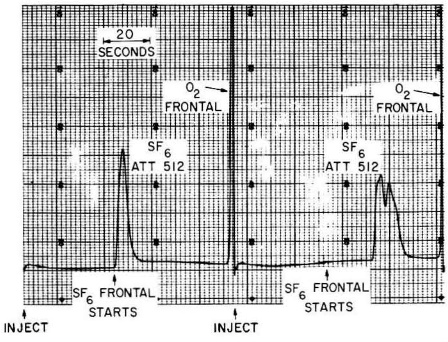


Figure 5. Frontal chromatograms of plume crosswind SF_6 determinations at LILCO Northport station

Plane flew perpendicular to the plume 1.6 km downwind at an altitude of 275 m (left) and 260 m (right). The early portion of the left profile was lost

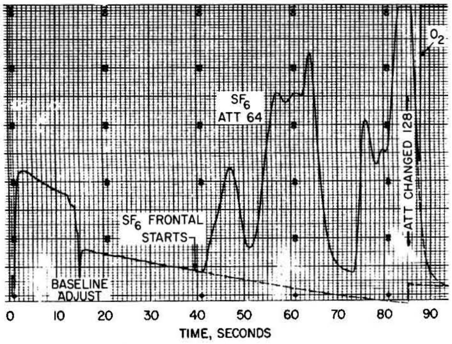


Figure 6. Frontal chromatogram of plume crosswind SF_6 determinations at Pennelec Keystone station

12 km downwind at an altitude of 914 m during unstable meteorological conditions with an SF_6 release rate of 114 scfh

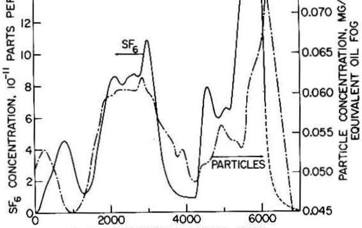


Figure 7. SF_6 and particle concentration vs. plume crosswind distance. SF_6 concentration determined from chromatogram of Figure 6

results shown in Figure 7, it was estimated that crosswind concentration gradient determinations at 10 times background should be attainable to about 100 km at a release rate of 100 scfh of SF_6 during unstable meteorological conditions. Details of the use of the real-time SF_6 sniffer in plume studies and ground level determinations will be presented in a future paper.

Conclusions

The laboratory chromatographic techniques developed here provided the direct determination of SF_6 at concentrations lower than previously attained without preconcentration and gave increased accuracy and stability because the SF_6 was eluted first from the column with the remaining constituents of the air sample having been backflushed.

As modified for real-time determination of SF_6, the portable electron capture chromatograph should significantly improve the ability to determine, define, and predict the complex nature of dispersion from single point sources, tall stacks, cities, and highways. Any air masses spiked with SF_6 could be traced for great distances, both in the air and on the ground; if sensitive, real-time portable instruments for SO_2, sulfate, or nitrogen oxides were used in conjunction with the SF_6 sniffer, information on the extent and rate of dilution, dispersion, chemical reaction, or fallout of the pollutant could be obtained. For example, in plume studies at short distances from the stack (<10 km) where the correction for background concentrations is negligible or can be determined, the rate of chemical conversion of nitric oxide could be obtained from the change in the nitric oxide to SF_6 ratio at various distances downwind from the stack. Having determined the rate of reaction, measured NO-to-SF_6 concentration ratios downwind (>15 km) at ground level would indicate what fraction of the nitric oxide concentration at that point could be attributed to the power plant plume. Similarly, the SF_6 sniffer could demonstrate whether or not a nuclear power plant stack effluent meets AEC ground level radioactive exposure doses. Not only would time averaged results be obtained, but the instrument would also aid in determining and evaluating short time exposure to high level doses or concentrations.

Acknowledgment

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Decomposition Rates of Ozone in Living Areas

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The role of photochemical oxidants as significant ambient air pollutants has long been recognized. The extensive literature concerning these pollutants is well documented and summarized in the Air Quality Criteria for Photochemical Oxidants (U.S. Dept. of HEW, 1970). While the pathways leading to the photochemical generation of ozone have been well delineated, the fate of ozone once it enters typical living spaces has only recently received attention. The current situation is succinctly stated in a literature review on Indoor-Outdoor Air Pollution Relationships by Benson et al. (1972): "considering the importance of the problem, very few data have been gathered on the presence, concentration, and generation of pollutants in indoor environments and on the penetration of pollutants from the outdoor environment into buildings."

Ozone in enclosed living areas originates from the infiltration of outdoor air and from various devices located inside which generate ozone by design or as an inadvertent by-product. The Canadian Standards Assn. has issued a regulation limiting the production of ozone by devices intended for household use (CSA, 1970). The Canadian regulation specifies that ozone concentrations shall not exceed 4 pphm (parts per hundred million by volume) during a continuous 7-hr test in a closed room of specified volume. The importance of ozone as an indoor air pollutant has also been recognized by the Food and Drug Administration. This agency has proposed a regulation limit-

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■ The decomposition rate of ozone has been monitored in several metal test facilities, an office, and a home. Experimental data generated in four test situations indicate that the decomposition of ozone in living areas follows first-order kinetics. The rate of ozone decay was very sensitive to variations in temperature, relative humidity, prior exposure of metal surfaces, and the number of potentially active catalytic surfaces in the room. Decay rates in closed areas can be enhanced by raising the temperature or increasing relative humidity. Activated carbon was shown to be effective as a decomposition filter for keeping ozone concentrations to acceptable levels in living areas.

ing the emission and accumulation of ozone to 5 pphm in the atmosphere of living and working space (*Fed. Regist.*, 1972).

The level of ozone that accumulates in an interior environment depends on a number of factors including the generation rate, decomposition rate, leakage, ventilation, and degree of mixing. Reasonable values for the decomposition rate constant must be known for various residential and office situations if reliable concentration predictions are to be made. Knowledge of the decomposition rate is essential if one is required to calculate generation rates from monitored concentration data. The experiments to be reported here were undertaken to determine decomposition rate information for various living-space situations of practical interest.

After completion of this work, we became aware of two additional comprehensive investigations on the decay of ozone indoors. Shair (1972) has proposed a ventilation model for predicting interior ozone levels given outdoor levels, decomposition rate constants, and flow rates. An independent study by Sutton and Nodolf (1972) revealed that ozone levels in a closed residence are significantly lower than the normal range of outdoor ozone concentrations.

Analytical Methods

Ozone concentrations were continuously monitored with a Mast Ozone Meter (Model 724-2) for the four test situations described in the Experimental Results section. For ozone decay studies in the stainless steel test room and home environment, a MEC chemiluminescent ozone detector (Model 1100-3, McMillan Electronics Corp.) was employed in addition to the Mast instrument. The Mast meter employs a coulometric ozone sensor with a potassium iodide reagent (for performance data, see Potter and Duckworth, 1965), and the MEC meter measures ozone concentrations by the photometric detection of chemiluminescence produced when ethylene gas reacts with ozone. The coulometric method is sensitive to other gaseous pollutants such as NO_2 or SO_2 which can oxidize or reduce the potassium iodide reagent to give erroneous readings, while the chemiluminescence detection method is professed to be free from interference and specific for ozone (Hodgeson et al., 1971).

The chemiluminescent ozone detector was calibrated using a stable ozone source and the neutral buffered potassium iodide procedure as specified by EPA (*Fed. Regist.*, 1971). After standardization, the MEC ozone meter was compared to the Mast coulometric detector. Over a concentration range of 2–42 pphm, ozone levels measured by the MEC meter were consistently higher by a factor of 1.3.

Temperature and relative humidity values were obtained in the various facilities by the use of a Bendix Hygro-Thermograph (Model 594) that was checked periodically with a sling psychrometer (Taylor Instruments). Data obtained in the home situation were confirmed by additional measurements with a Honeywell Humidity and Temperature meter (Model Y477A).

Experimental Results

Experiments in Aluminum Odor Test Facility. The initial ozone decomposition experiments were conducted in an aluminum odor test facility. This chamber has a volume of 76.6 ft^3, an area of 121 ft^2, and a surface-to-volume ratio of 1.6 ft^{-1}. Construction details on this chamber have been described previously by Mapes and Vance (1971). A small positive corona ionizer was installed in the exterior loop of the test facility. Air from the main chamber was circulated through the ionizer operated at approximately 10.5 kV until the desired ozone level was obtained. The ionizer was then electrically deactivated, and the ozone concentration in the main chamber was monitored continuously during the decay period.

Initial concentrations of ozone (C_0 = 20–200 pphm) employed in these first experiments in the clean test chamber were higher than those encountered in living areas. Certain conclusions drawn from these high-concentration experiments were of much value in planning the living area studies. The findings were as follows:

The decomposition of ozone in the clean, all-aluminum system follows a simple first-order rate equation. The order of the decomposition reaction was determined by consideration of the pertinent partial reaction time ratios. The $t_{1/2}/t_{1/3}$ ratio was determined for some seventeen runs in the test facility. The average value for this ratio was found to be 1.70 ± 0.05. The theoretical value of this ratio should be 1.701 for a first-order rate process (Benson, 1960). The $(t_{3/4} - t_{1/2})/t_{1/2}$ ratio was also calculated for the same seventeen runs. The average value for this ratio was 0.92 ± 0.08; the theoretical value for the latter ratio is 1.00 for a first-order process (Benson, 1960).

The decomposition rate was found to be strongly dependent on the extent of prior exposure of the wall surface to ozone. The decomposition rate constant decreased by a factor of about five with progressive seasoning of the aluminum surfaces. This effect of seasoning on decomposition rate is demonstrated in Figure 1. The aluminum chamber regained part of its initial activity for destroying

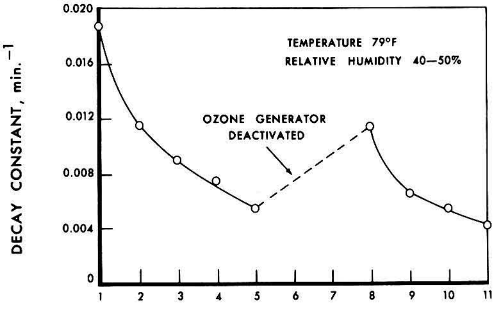

Figure 1. Effect of seasoning on decomposition rate of ozone in an aluminum chamber

ozone when exposure to this pollutant was discontinued over a weekend.

The ozone decomposition rate constant was found to be highly dependent on the relative humidity of the test chamber air. The calculated rate constant increases dramatically with increasing humidity; this dependence on humidity is illustrated in the data of Table I.

Decomposition Experiments in Metal Test Rooms. The second set of decomposition experiments was performed in an aluminum test room (420 ft^3) and a stainless steel test room (525 ft^3) specifically designed for pollutant removal studies. For runs in these small test rooms, ozone was generated by continuous operation of a commercially available home-type electronic air cleaner. Such air cleaners are normally provided with an activated carbon filter downstream from the electronic filter. For these tests the carbon filter was purposely removed to permit the attainment of higher ozone levels. The generator was electrically deactivated when the ozone level reached a concentration of about 9.0 pphm. The air circulation rate was maintained at 300 ft^3/min (cfm), and the ozone concentration in the test rooms was continuously monitored until it had dropped to a level of about 0.5 pphm. A surface-to-volume ratio was calculated for each of the metal test rooms allowing for the presence of the air cleaner: aluminum = 1.0 ft^{-1}, stainless steel = 0.82 ft^{-1}.

To demonstrate the efficacy of activated carbon as an ozone decomposition catalyst, several additional runs were made in the test rooms. In these runs granular activated carbon filters were interposed in the circulating airstream during the decomposition phase. Decay rate data showing the beneficial effect of activated carbon in decomposing ozone are given in Table II. A typical plot is shown in Figure 2. The introduction of the carbon filter reduced the ozone half-life by an order of magnitude.

To evaluate the reproducibility of the rate data, the decomposition of ozone was repeated on the same day and on different days with a carbon filter in the air cleaner. Three runs on the same day in the aluminum room gave a coefficient of variation equal to 2.4%. Seven separate determinations on different days in the stainless steel room yielded a coefficient of variation of 5.2%. The slight variation in the values of k attest to the constancy of the ozone decomposition rate in sealed metal rooms with temperature constant and relative humidity varying only slightly.

The decrease in the rate of ozone decomposition with time of exposure as cited for the aluminum chamber was confirmed by tests in the stainless steel room. Over a five-day period of consecutive analysis the decay rate constant diminished in value from 0.025 to 0.013 min^{-1}.

Decomposition Experiments in Office Area. Prior to undertaking off-site experiments in a real home situation, a series of runs was carried out in a typical office. The office employed had a volume of 1950 ft^3 and is believed to be fairly representative of offices in commercial situations. The walls were painted steel partition panels and the floor was of vinyl tile construction. Normal office accouterments such as desk, chairs, file cabinets, and books were all present. A surface-to-volume ratio for the office was estimated to be 0.86 ft^{-1}. This value was calculated by considering each piece of furniture as a rectangular parallelepiped. There were no windows in this office and ventilation ducts were closed during the test. The sampling tube of the Mast monitor was positioned in the center of the floor at a height of 27 in.

Table I. Effect of Relative Humidity on Ozone Decomposition in Aluminum Chamber

Volume of chamber = 76.6 ft^3

R. h., %	Temp, °F	First-order decay const, min^{-1}	Half-life, min
5	72.2	0.0014	495
28	78.8	0.0015	462
48	80.0	0.0029	239
55	80.0	0.0034	204
66	79.2	0.0060	115
87	79.2	0.0574	12.1
87	79.2	0.0541	12.8

Table II. Summary of Rate Constants Obtained in Various Enclosed Areas

Flow Rate = 280–300 cfm
Temp = 70–80°F
r.h. = 26–50%

Test area	First-order decay const, min^{-1} [a]	Half-life, min
Decay of ozone in room without carbon filter		
Aluminum room, 420 ft^3	0.054 ± 0.004	13
Stainless steel room, 525 ft^3	0.025 ± 0.002	28
Bedroom, 1440 ft^3	0.121 ± 0.004	5.7
Office, 1950 ft^3	0.063 ± 0.002	11
Decay rate with activated carbon filter in air cleaner		
Aluminum room, 420 ft^3	0.465 ± 0.010	1.5
Stainless steel room, 525 ft^3	0.323 ± 0.016	2.1
Bedroom, 1440 ft^3	0.225 ± 0.018	3.1
Office, 1950 ft^3	0.108 ± 0.008	6.4

[a] Rate constant with 95% confidence limits.

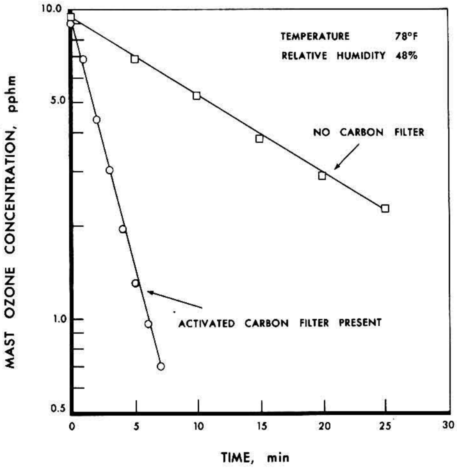

Figure 2. Ozone decomposition in an aluminum room

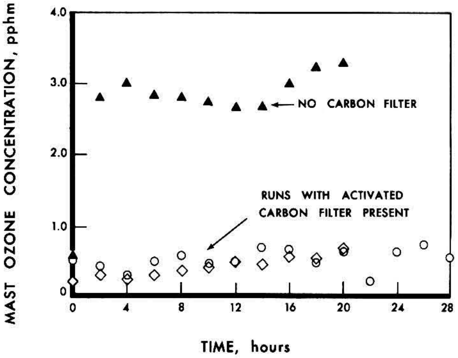

Figure 3. Ozone levels attained during extended runs in office area

As in previous studies the air cleaner was operated without the carbon filter in place until the desired ozone level was obtained in the office. The ionizer circuit was then deactivated, but the air recirculating blower was allowed to operate throughout the monitored decay period. Decomposition rates in this office situation are presented in Table II.

While decomposition rate data were the main objective in these experiments, some interesting steady-state concentration information was developed in long-term runs in this office situation. In a 20-hr run with the carbon filter removed the average Mast reading was 3.00 ± 0.05 pphm and the maximum concentration noted during the 20 hr was 3.45. In an analogous 21-hr run with the carbon filter in place the average was 0.40 ± 0.15 pphm and the maximum noted was 0.70 (Figure 3).

Decay of Ozone in a Home Environment. The site chosen to monitor ozone decomposition in a home was a 1440-ft^3 bedroom (13 ft 6 in. × 13 ft 4 in. × 8 ft). The room contained twin beds, two end tables with lamps, a chest of drawers, and a valet. The bedroom located at the southeast corner of the house had two windows with shades and curtains. Warm or cool air was supplied via two inlet registers and vented through a single return register. The painted room had hardwood floors partially covered by a cotton area rug. During ozone decay runs the entry door, closet doors, and windows were closed. As mentioned in prior studies, ozone was generated by an electrostatic precipitator which was deactivated once a steady-state level was approached. It was difficult to produce ozone levels above 3 pphm in the bedroom, and in some cases, an additional electronic air cleaner and an ultraviolet lamp were employed as auxiliary ozone generators. The surface-to-volume ratio for the bedroom was found to be 0.99 ft^{-1} by assuming that each accessory could be evaluated as a rectangular parallelepiped as was done for the office. This is definitely an estimate of the true area since the bedroom contained irregular-shaped objects, and porous surfaces such as drapes, rugs, and bedspreads.

In the initial decay experiments, one inlet register and the return register were left open with the furnace off to simulate typical room conditions without external ventilation. There was some air leakage from the room but no more than would be found in a closed bedroom with an occupant at rest for the night. The decrease of ozone concentration with time followed first-order kinetics as found in previous studies. The effectiveness of activated carbon in enhancing the decomposition of ozone was noted in earlier studies and was confirmed in the bedroom experiments (Table II). The ozone concentration remained below 1.0 pphm during 50 hr of continuous operation with a carbon filter downstream of the generator. The rate of ozone decay was significantly lowered by turning off the air cleaner used as a source of airflow in the bedroom. This result is reasonable since operation of the blower would favor mixing of ozone with other contaminants in the gaseous phase and would speed the movement of ozone to surfaces in the room.

A series of decay runs was performed in the closed room to determine the temperature dependence of the ozone decomposition. For these tests, all registers were closed and sealed with cardboard and masking tape. Ozone concentrations were monitored by the chemiluminescent detector as well as the Mast coulometric technique. A comparison of rate constants calculated from data generated by the two different instruments is given in Table III. The good agreement between rate constants calculated from data generated by the two different instruments is supporting evidence for prior experimentation performed using only the Mast Meter.

It is possible to obtain Arrhenius type plots (Figure 4) from the data given in Table III. The slopes of the straight lines obtained from a least-squares fit of the data can be utilized to calculate an apparent activation energy, E_a, for the ozone decomposition reaction occurring in the bedroom under study.

$$\ln k = \frac{-E_a}{RT} + \ln A \qquad R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

The slope of the straight line obtained from MEC data gives an E_a value of 6.4 ± 1.3 kcal/mol at an airflow of 290 cfm and a value of 6.7 kcal/mol at zero airflow (note only two data points). The E_a equals 8.0 kcal/mol using the slope of the line from Mast data. The agreement of E_a values from data generated by two different ozone meters lends some credence to the validity of the numbers. The values of E_a are questionable, however, mainly due to the narrow temperature range studied, and the large number of possible interfering variables. One might speculate that the relatively low values of E_a suggest a surface reaction, but it is difficult to assess the effect of organic molecules or other pollutants (SO_2) in the gaseous phase that might decompose ozone.

Discussion

The salient observations made in this investigation of ozone decomposition in living areas can be summarized in the following statements:

- The decomposition of ozone was found to follow first-order kinetics in an aluminum chamber, an aluminum room, a stainless steel room, an office, and a bedroom.
- The rate of ozone decay was dramatically altered by variations in humidity or temperature. Increasing either the humidity level or the temperature enhanced the rate of ozone decay.
- The rate of decomposition in an aluminum

Table III. Variation of Ozone Decay Rate with Temperature as Determined by Two Different Ozone Monitors

Air flow in electronic air cleaner, cfm	Temp, °F	R. h. %	First-order rate const, min^{-1} From Mast data	First-order rate const, min^{-1} From MEC data
0	52.5	43	0.067 ± 0.001	0.070 ± 0.003
0	78	43	—	0.124 ± 0.008
290	48	37	0.107 ± 0.001	0.113 ± 0.002
290	51	42	0.100 ± 0.001	0.111 ± 0.002
290	57.5	50	0.110 ± 0.01	0.121 ± 0.003
290	69	46	0.160 ± 0.009	0.162 ± 0.004
290	78	43	—	0.192 ± 0.003

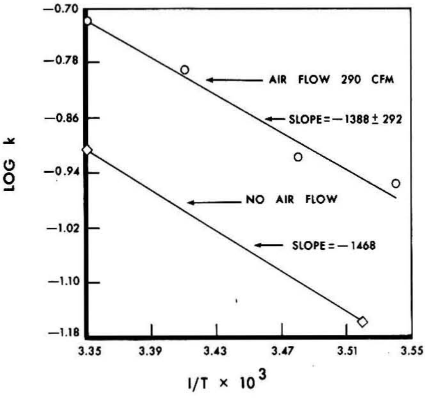

Figure 4. Arrhenius plot of data from MEC chemiluminescent detector

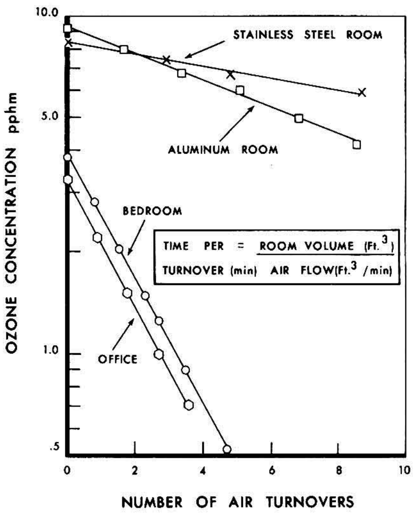

Figure 5. Decrease in ozone concentrations as a function of air turnovers with no carbon filters present

Table IV. Change in Ozone Concentration after Two Turnovers as a Measure of Ozone Removal Efficiency

Test area	Temp, °F	R.h., %	$(C_0 - C_2)/C_0{}^a$ Without carbon	With carbon filters
Aluminum, 420 ft^3	80	55	0.17	0.68
Stainless steel, 525 ft^3	78	66	0.08	0.65
Bedroom, 1440 ft^3	70	56	0.56	0.72
Office, 1950 ft^3	80	26	0.59	0.79

[a] The air cleaner provided a flow rate of 280–300 cfm to circulate air in the rooms. If perfect mixing is assumed, the time to effect one turnover is equal to the room volume divided by the flow rate. C_2 represents the concentration after two turnovers.

chamber and stainless steel room decreased with continuous exposure to ozone. The metal surfaces appeared to become seasoned toward this oxidant.

- The half-life of ozone in a typical bedroom was rather short (6 min) suggesting that this pollutant decomposes rapidly after it enters typical living spaces.
- Activated carbon was shown to be effective in removing ozone from a flowing airstream. The carbon filter increased the rate of decay and lowered steady-state ozone levels in a closed room when placed directly downstream from an electrostatic precipitator.

Factors that can influence ozone decay include the catalytic nature of surfaces or gaseous species present in the room, the effective surface area available for decay, and the efficiency of mixing in the room. It is difficult to compare directly the rate constants in the various facilities due to differences in room volume. To overcome this problem one can consider the decrease in ozone concentration per turnover of air volume (Figure 5). The loss of ozone after two turnovers was chosen to calculate a relative efficiency rating for destroying ozone (Table IV). By use of this approach, it becomes evident that ozone decomposition is much more rapid in the office and bedroom than in the metal test rooms. This is expected since the living areas contain a wealth of potential active sites for ozone decay such as painted walls, furniture, books, drapes, etc. With carbon present in the airstream the values for the several rooms are more consistent, suggesting that a considerable amount of ozone decomposition is occurring at the activated carbon surface. It is obvious that the apparent rate of decay will be influenced by leakage or air exchange with the test facility. While efforts were made to minimize this effect, it was much more difficult to achieve this isolation for the office and home experiments.

Ozone present in indoor living areas can decompose by homogeneous reactions in the gas phase or by heterogeneous reactions with surfaces present in the enclosure (Benson, 1960). The loss of ozone by a thermal decomposition or photolysis reaction should be minimal because of the relatively low temperatures and the absence of any high-intensity light source. Catalytic reactions are of great importance in low-temperature atmospheric reactions and may account for the rapid decay of ozone found in a bedroom. The relatively low estimate of the activation energy for ozone decay found in the bedroom study suggests a surface reaction, but a more controlled experiment performed over a greater temperature span is required to elucidate fully the mechanism.

The rate constants in Table II for the ozone decay without activated carbon can be expressed in units of volume per unit area per unit time to permit comparison with other workers in the field (Shair, 1972; Sutton and Nodolf, 1972). The first-order decay constants in units of ft^3/ft^2-min are: aluminum room 0.054; stainless steel room, 0.031; office 0.073; bedroom, 0.122. The actual values of the rate constants in these units for the office and bedroom may be less than given here due to the impossibility of measuring true surface area in real living spaces.

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Concentrations, Decay Rates, and Removal of Ozone and Their Relation to Establishing Clean Indoor Air

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■ Transitory concentrations of ozone, within typical buildings located in photochemically smoggy areas, were found to lag in time and to be only a little less in value as compared to corresponding outdoor concentrations. The ozone decomposition within buildings involved a heterogeneous mechanism. Decomposition rate constants for several common surfaces were found to range in value from about 10^{-1}-10^{-3} ft^3/ft^2-min. Rubber, fabrics, and plastics appeared to decompose ozone much more rapidly than metals and glass. All materials demonstrated a reduction in the rate constant in extended use. One material, plywood, showed some recovery after a two-day exposure to an ozone-free atmosphere. Experiments indicated that certain filters, expecially activated charcoal, can be used to reduce indoor levels of ozone well below the maximum acceptable limits. Calculations, based upon a "stirred-tank" reactor model, yielded results similar to those observed with respect to transitory indoor vs. outdoor concentrations of ozone.

The notoriety of the polluted air in the Los Angeles Basin is certainly widespread, and active programs are being undertaken to improve the quality of the atmosphere. Nevertheless, even the most optimistic forecasts envision periods of five to ten years ("Profile of Air Pollution Control," 1971) before any significant improvement might be realized. It seems warranted, therefore, to spend some effort on the development of devices and/or procedures which will at least alleviate the adverse effects of air pollution even though they do not eliminate the sources of smog.

The smog-infested areas such as the Los Angeles Basin are by their nature city areas of high population density, and the average citizen in such areas is likely to spend by far the largest portion of his time inside buildings. Kalika et al. (1970) suggest that the average person spends about 80% of his time indoors. It follows that the exposure of most individuals to smog could be reduced drastically if these buildings could be maintained at a low level of pollution. One might look then to a building not only for protection from rain, heat, and cold but also for protection from polluted air.

As emphasized by Kennedy (1970), much has been written concerning various indoor environmental factors such as temperature, humidity, air velocity, ventilation rates, odor, dust, and air ions; but relatively little has been written with respect to indoor pollution levels. An excellent literature survey on indoor-outdoor air pollution relationships was published recently by Benson et al. (1972); virtually all this work has been concerned with SO_2, CO, CO_2, and /or various types of particulate matter. Surprisingly little work has been done with respect to components generally associated with photochemical smog. Some time ago Richardson and Middleton (1958) determined the interrelationship between ventilation and air monitoring by use of questionnaires concerning eye irritation. More recently, Thompson (1971) studied the relationship between indoor and outdoor oxidants in hospitals located in Riverside, Calif. No systematic studies have yet been reported concerning the relationship between the indoor vs. outdoor concentrations of ozone in photochemically smoggy areas; associated with such studies would be a determination of the mechanism and rate by which ozone decomposes indoors. Near the end of this present work, we were informed that studies of ozone decomposition were being performed independently in another laboratory (Mueller et al. 1973).

The most significant air pollutants in the Los Angeles Basin are ozone, carbon monoxide, oxides of nitrogen, oxides of sulfur, hydrocarbons, and particulates. A first stage smog alert may be called in Los Angeles County when the concentration of carbon monoxide reaches 50 ppm, when the concentration of nitrogen oxides reaches 3 ppm, when the concentrations of sulfur oxides reach 3 ppm, or when the concentration of ozone reaches 0.5 ppm for a minimum of 5 minutes duration ("Profile of Air Pollution Control," 1971).

The smog alert system was adopted in Los Angeles June 20, 1955. Up to January 1971, 80 smog alerts were declared; these were all based upon ozone. The carbon monoxide alert level was changed from 100-50 ppm on December 17, 1970. Since then, at least 3 first-stage alerts have been declared on the basis of carbon monoxide. However, most of the smog alerts are still called on account of ozone. The California State Air Quality Standard for oxidant is 0.10 ppm averaged over a 1-hr period. From 1955 until 1971, the ozone level within the LA basin reached 0.1 ppm or above during 288 days for the average year, and 218 days during 1971. Figure 1 shows the number of

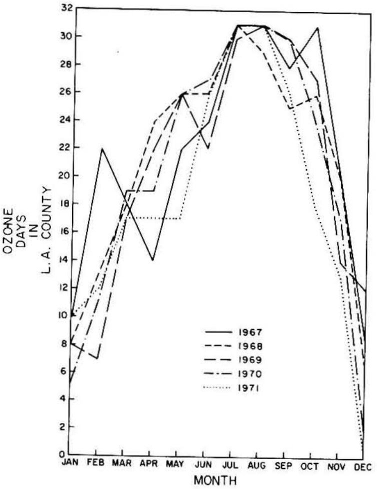

Figure 1. The number of days each month in LA County, over the last five years, during which the ozone concentration has risen to 0.1 ppm or above

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days each month, over the last five years, during which the ozone concentration has risen to 0.1 ppm or above; there have been at least 16 "ozone days" per month during at least eight months each year during the last five years.

Although ozone was once considered as a health aid, it is one of the strongest oxidants known and is now considered to be quite toxic. The work up to 1953 concerning the pharmacological properties of ozone was extensively reviewed by Thorp (1954). The work up to 1969 was critically reviewed by Mueller and Hitchcock (1969); their general conclusions regarding exposure to ozone are: The lungs and senses are primarily affected, there is impairment of pulmonary function in humans at concentrations found in polluted areas, ozone tends to oxidize the lung tissue in animals, and ozone increases susceptibility to respiratory infection.

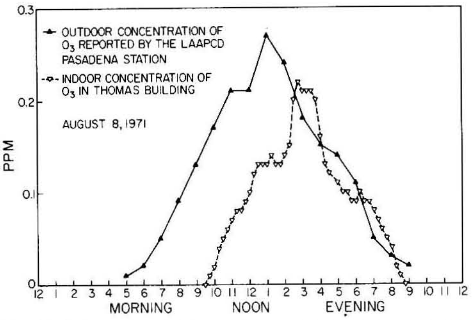

Figure 2. Ozone concentration vs. time of day for Thomas Building, August 8, 1971

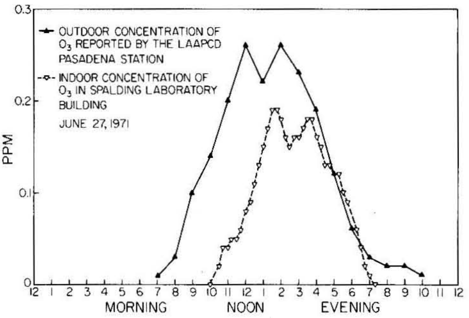

Figure 3. Ozone concentration vs. time of day for Spalding Laboratory Building, June 27, 1971

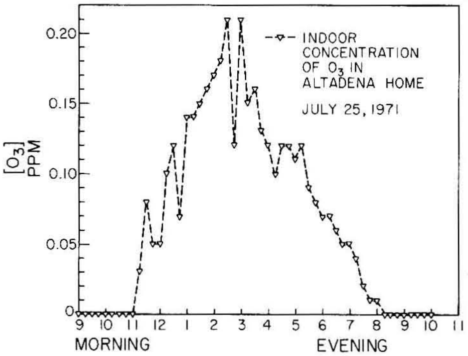

Figure 4. Ozone concentration vs. time of day in private home in Altadena, July 25, 1971

With these thoughts in mind, a program aimed at the investigation of air quality inside buildings was initiated with attention directed initially at ozone. Three sets of experiments were performed using a Dasibi Corp. Model 1003 ozone monitor. First, the ozone levels were determined within selected buildings during smoggy days. Next, the general mechanism through which ozone decays within buildings was established and rates of ozone decomposition were measured. Next, air filters were tested with respect to their effectiveness in destroying ozone. Finally, a theoretical model was developed to permit the correlation of indoor vs. outdoor concentrations of ozone as a function of time.

Ozone Concentrations in Office Buildings

Ozone concentrations in two adjacent campus lab-office buildings were monitored and compared with the outside values. The air-conditioning system in the first building supplied the ventilation ducts with 100% outside air. The peak ozone levels within the first building were about 80% ± 10% of the outside levels; typical daily profiles are shown in Figures 2 and 3. The air-conditioning system in the second building supplied the ventilation ducts with approximately 70% of outside air and recycled about 30% of the exhaust air. The peak ozone levels within the second building were about 65% ± 10% of the outside levels. To check the applicability of the APCD (Air Pollution Control District, County of Los Angeles) measurements, made about 500 yd from the two office buildings, the ozone concentrations were measured immediately outside of the two adjacent buildings. Although the APCD values were generally slightly higher than those immediately outside of the office buildings, both sets of values agreed to within 20% of each other during most of the day. Actually the ventilation rates associated with these buildings were not measured; however, they could be estimated to supply about 10 times the building volume per hour. These results are perhaps not surprising, but they do indicate that the residence times associated with typical ventilation systems are not long enough to allow the ozone levels inside buildings to decay to levels much lower than the outside values.

Ozone Concentrations in Private Residences

Measurements were obtained in a typical private residence with carpeted floors, draped windows, and a fair amount of overstuffed furniture. In this test the ventilation system was off, several windows were open, and the doors were opened periodically as persons entered and left the dwelling. Typical results are shown in Figure 4. Spot measurements of the outdoor concentrations indicated that the maximum indoor concentrations of O_3 were about 0.7 those of the outside, and that these maxima lagged those of the outside by about 1 hr.

Additional experiments were performed in which a house was filled completely with outside air and then isolated from the outside as much as possible; after filling the house with outside air, all windows and doors were closed. In the first experiment, persons walked through various rooms in normal activity but there was no forced internal circulation of air: in this case the ozone decayed exponentially in time from an initial concentration of 0.23-0.04 ppm in 30 min. In the second experiment, the air was circulated by means of an internal circulation system involving only ordinary glass fiber filters; in this case the ozone decayed exponentially in time from 0.23 ppm initially to 0.03 ppm in about 20 min (Figure 5).

Although the above series of tests involving private residences was of an exploratory nature, it did lead to a number of definite conclusions as to the behavior of ozone inside dwellings. Perhaps the most pertinent one is the fact that, even without special provisions, the ozone level within a home decreases at rather rapid rates once the doors and windows are closed. The infiltration rate during the above test was believed to be small, and was not measured.

Characterization of Test Chamber

Several exploratory experiments were conducted in rooms of various sizes. The ventilating registers were closed off and infiltration was reduced to a minimum. These tests clearly indicated that the ozone decay rate was directly related to the surface-to-volume ratio. Furthermore, the ozone decayed exponentially in time with rates which were essentially independent of the amount of mixing of the air. (The mixing was accomplished by several large fans located throughout the enclosed room.) Consequently, the room data could be interpreted within the framework of heterogeneous reaction rates, with decay constants, K, ranging from 0.05–0.14 ft^3/ft^2-min.

To study the decay processes under better controlled conditions, a test chamber was constructed. In most of the experiments reported below, the temperature of the system was maintained at 72 ± 1F°, and the relative humidity of the air was maintained at 50 ± 5%.

A test chamber, having dimensions 48 × 48 × 63 in. was constructed from acrylic Lucite (polymerized methyl methacrylate) sheets of 0.090 in. thickness. The chamber had a surface area of 106 ft^2, a volume of 84 ft^3, and a surface to volume ratio of 1.26 ft^{-1}.

The ozone decay characteristics of the test chamber had to be ascertained first, so that the results could be interpreted properly when investigating the effect of various test surfaces to be placed inside the chamber. The decomposition rate of the plain chamber appeared to be first order with respect to the concentration of ozone. However, the rate constant decreased with increasing exposure to ozone. As shown in Figure 6, the decomposition rate constant, initially was above 10^{-2} ft^3/ft^2-min for the "fresh" chamber, decreased relatively rapidly during the first 500 min of use, and then continued to decrease slowly as the chamber "aged." The rate constant is currently below 10^{-3} ft^3/ft^2-min after about 10^4 min of use. Discontinuities were observed in the "rate constant" vs. "usage time" when the initial concentration of ozone was raised above that commonly used; these discontinuities suggest that "surface aging" may be some function of the exposure level and the time of exposure. (Incidentally, similar aging phenomenon may occur on the walls of smog chambers used to study outdoor smog chemistry.) One set of experiments, wherein the relative humidity within the empty chamber varied from 15–90%, indicated little influence of the relative humidity upon the rate constant for Lucite. In the case of aluminum, on the other hand, the rate constant is greatly influenced by the relative humidity (Mueller, 1972).

Ozone Decay Rates on Several Common Surfaces

Several materials in common use were tested within the Lucite chamber. Generally the test samples were 3 × 4 ft in size, thus providing 24 ft^2 of total surface area. As shown in Table I the rate constants, associated with the materials studies, varied from about 0.2 ft/min to about 10^{-3} ft^3/ft^2-min.

Eight runs were conducted with a neoprene sheet (having a thickness of ⅛ in. and a total surface area of 14 ft^2); runs 1, 5, and 8 are shown in Figure 7. It can be seen, that the rate constants varied from ~0.19 to 0.03 ft^3/ft^2-min. As indicated in Figure 8, the neoprene aging curve is similar to that of Lucite (Figure 6); however, the values of K were much higher for neoprene and reached a plateau

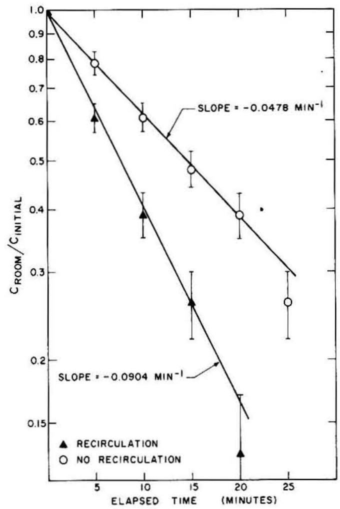

Figure 5. Ozone concentration vs. time for home with and without internal recirculation: No filters

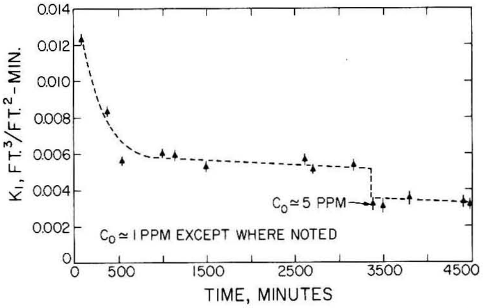

Figure 6. Rate constant vs. exposure time for Lucite test chamber

Table I. Measured Values of Ozone Decomposition Rates for Several Common Surfaces

Material	K, ft^3/ft^2 − min
Cotton muslin	0.214 → 0.029
Lamb's wool	0.208 → 0.008
Neoprene	0.19 → 0.03
Plywood (1 side varnished)	0.06 → 0.01
Nylon	0.063 → 0.001
Polyethylene sheet	0.048 → 0.020
Linen	0.0185 → 0.0107
Lucite	0.012 → 0.001
Aluminum	0.002 → 0.001
Plate glass	0.002 → 0.001

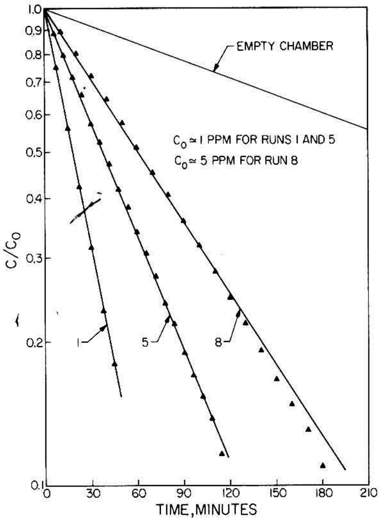

Figure 7. Typical rate data obtained from test chamber experiments: Neoprene ⅛ in. thick and 14 ft^2 of total surface area

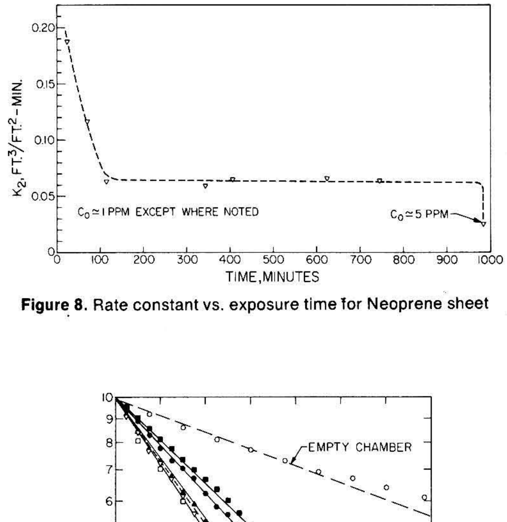

Figure 8. Rate constant vs. exposure time for Neoprene sheet

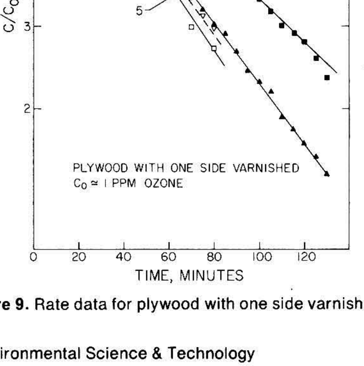

Figure 9. Rate data for plywood with one side varnished

much more rapidly than those for Lucite. Nylon had in intermediate values of the rate constant which again decreased in later tests. The rate constants of polyethylene sheet (0.004 in. thick) and linen were also in the intermediate range and showed a decrease with long term exposure to O_3. Aluminum and plate glass indicated relatively low values of rate constants, and that for aluminum is in qualitative agreement with the statement by Mittler et al. (1959); their toxicity test chamber was "lined with aluminum sheet to prevent undue decomposition of ozone . . . ."

Plywood (¼ in. thick) led to an intermediate decomposition rate and the application of varnish did not produce a significant change. Tests repeated in quick succession indicated the decrease in the value of K as had been observed with other materials. Runs 1, 2, and 3 were conducted during the same morning. Runs 1, 4,and 5 were conducted during the mornings after time intervals of two days. However, in the case of plywood the value of K returned to its original value after a few days with no ozone exposure (Figure 9).

These results suggest that an irreversible chemical reaction, "aging," is occurring with a time constant much longer than that associated with the intermediate decay of ozone. To understand the detailed mechanisms of ozone decay on common surfaces, additional studies will have to be conducted. It will also be of interest to determine why some materials appear to be able to reverse the aging process during time intervals of the order of a day.

Homogeneous Decomposition of Ozone

Benson and Axworthy (1959) reviewed the kinetic data concerning the gas phase decomposition of ozone; they concluded that most of the known data on the homogeneous thermal decomposition of ozone can be explained quantitatively in terms of the following steps:

$$O_3 + M \underset{2}{\overset{1}{\rightleftharpoons}} O_2 + O + M \qquad (1)$$

$$O + O_3 \rightarrow 2O_2 \qquad (2)$$

The symbol M represents a suitably weighted sum of all the substances, including O_3, present in the gas. At concentrations of O_3 in smoggy air the half-life of ozone, relative to the first step in the above sequence, is of the order of 10^3 hr (for example, see p 152 of Leighton, 1961). Ozone is also inactive in the gas phase with respect to CO (Zatsiorskii et al., 1940) and with respect to SO_2 (Cadle, 1956). On the other hand, O_3 reacts quite rapidly in the gas phase with NO, NO_2, and olefins (for example see Chapter 7 of Leighton, 1961). Ozone decomposition experiments, involving structures wherein NO, NO_2, and olefins were essentially absent, indicated decay rates to be much more rapid than would be predicted by known homogeneous mechanisms.

Heterogeneous Decomposition of Ozone

It has long been known that the decay of ozone is heterogeneous, and first order with respect to the ozone concentration when the ozone concentration is about 10^4 ppm and the reaction vessel is of laboratory size (Riesenfeld and Bohnholtzer, 1927; Riesenfeld and Schumacher, 1928; and Glissman and Schumacher, 1933). Harteck and Donders (1953) measured the heterogeneous decomposition rate of ozone (at concentrations near 10^4 ppm), in contact with glass wool, at 100°C; they proposed a decomposition mechanism in which O_3 is taken to be in thermal equilibrium with O_2 and O is the gas phase, and O atoms diffuse to the surface where they are destroyed.

Two arguments can now be used to demonstrate that the mechanism proposed by Harteck and Donders (1953) is invalid. As indicated previously, the work of Benson and Axworthy (1959) indicated that the homogeneous thermal decomposition of O_3 into O_2 and O is much too slow to permit equilibrium concentrations to develop. Furthermore, even if equilibrium among O_3, O_2, and O did somehow exist in the gas phase, it may be shown that the flux of O atoms colliding with the wall is orders of magnitude too low to account for the decomposition rates associated with all of the materials on which data were reported in the foregoing sections. In arriving at this conclusion, one may start by considering the maximum decomposition rate, K_m, associated with O atoms diffusing to the wall. This rate is equal to $(\bar{v}_O K_p)/4P(O_2)$ where $\bar{v}_O$ is the average velocity of O atoms, K_p is the usual equilibrium constant, and $P(O_2)$ is the partial pressure of O_2. In all of the present experiments (conducted with air near 75°F) $\bar{v}_O \simeq 1.2 \times 10^5$ ft/min, $K_p \simeq 2 \times 10^{-12}$ atm, and $P(O_2) \simeq 0.8$ atm, and $K_{m(O)} \simeq 7.5 \times 10^{-8}$ ft/min. As shown in Table I, measured decomposition rates of ozone, "K", ranged in value from $\simeq 0.2$ ft/min to 10^{-3} ft/min. The most obvious mechanism of the heterogeneous decomposition of ozone involves the diffusion of O_3 molecules to the surface where they decompose. In this case, the maximum decomposition rate, $K_{m(O_3)}$, is equal to $\bar{v}(O_3)/4$ where $\bar{v}(O_3)$ is the average velocity of O_3 molecules. For the present experiments $\bar{v}(O_3) \simeq 7.1 \times 10^4$ ft/min, and $K_{m(O_3)} \simeq 1.8 \times 10^4$ ft/min. This then leads to the conclusion that the reaction probability, $\gamma \equiv K_m/K_{m(O_3)}$ would have had values from 10^{-5} to 10^{-8}. Unfortunately reactive scattering experiments involving molecular beams of ozone impinging upon common surfaces, have not yet been reported; thus, as of now, we cannot compare these values of γ with more direct measurements. As far as we could determine, the closest experiment along these lines yet reported involved the surface reaction of ozone on clean (111)-oriented germanium single-crystal surface at temperatures ranging from 510–780°C (Madix et al., 1971); these authors found the values of γ are greater than 0.1 for temperatures between 780° and 550°C, and the value of γ decreased at least an order of magnitude between 550° and 510°C. This trend hints at the possibility that values of γ at room temperature may be much lower than 10^{-2} which would be in agreement with our conclusion.

Effectiveness of Various Filters in Destroying Ozone

In parallel with the experiments concerning the decay of ozone within enclosures, the effectiveness of a few air filters was determined. For this purpose a duct, 10 ft long and 1 ft² in cross section, was constructed so that various filters could be inserted into the channel at about the middle of the duct. Filters of activated charcoal, Purafil (potassium permanganate and aluminum oxide), and glass fibers were tested, as shown in Figure 10; for initial ozone concentrations below 1 ppm, the activated charcoal removed over 95% of the ozone up to the highest flow velocity of 300 ft/min. The results concerning activated charcoal are qualitatively consistent with conclusions drawn previously by Bush and Segall (1970) and by Haagen-Smit (1972). The Purafil filter removed a substantial, but lower fraction of ozone, and yielded results which are similar to those published previously (Purafil for Corrosion Control, 1971). The glass fiber material did not seem to have a measurable effect upon ozone; it is understood, of course, that the glass fiber filter was not designed for that purpose and was not expected to be effective against ozone.

One set of experiments was performed within a sealed room, while air was drawn through a filter and recirculated. As shown in Figure 11, some filters can greatly reduce the time required for the ozone to decay in typical rooms. No duration tests were made, but the data indicate that various filters may be of great help in lowering the concentrations of ozone indoors. These results are also consistent with the work of Thompson (1971) and Pfeiffer (1972).

Proposed Model Equation

The simplest ventilation model, which appears appropriate to consider, involves treating a room or the inside of a building as if it were a well-mixed chemical reactor. Then, a material balance for ozone yields the following expression:

$$V\frac{dC}{dt} = q_0C_o + q_1(1 - F)C_o - (q_0 + q_1)C - \sum_j K_jA_jC \quad (3)$$

where C is concentration of ozone indoors, C_o is concentration of ozone outdoors, t is time, V is volume of the

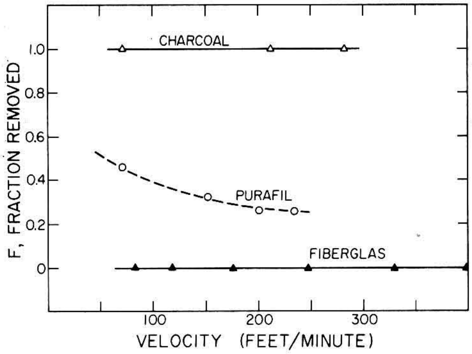

Figure 10. Fraction of ozone removed vs. velocity: For single pass through various filters

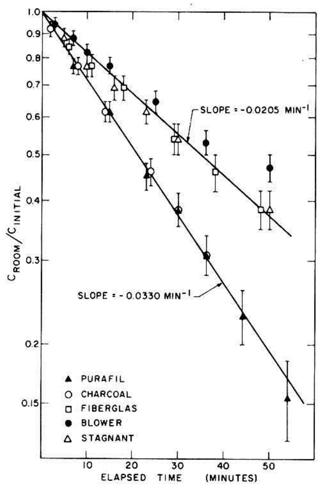

Figure 11. Decay of ozone in sealed room with recirculation through various filters and without

structure, q_0 is flow rate of air which does not pass through a filter, q_1 is flow rate of air which passes through a filter before entering the structure, F is fraction of ozone removed in the air stream passing through the filter, K_j is rate constant associated with the heterogeneous decomposition of ozone on the jth surface, and A_j is area of the jth surface.

The term on the left-hand side of the equation represents the accumulation of ozone within the structure. The first and second terms on the right-hand side of the equation represent inputs. The term q_0 includes infiltration, or leakage of air through the structure. The term q_1 will generally refer to the rate of ventilation which passes through a filter in the central system. The third term represents an outflow, and the last term represents the sink. The formulation can easily be extended to include internal recirculation, internal sources, volumetric reaction, etc.

The model equation was also used to interpret the experiments involving the Lucite chamber wherein various materials, in common usage, were tested. In this case $q_0 = q_1 = 0$, and the initial condition was $C = C_i$ at $t = 0$. The solution to the model equation then becomes

$$C/C_i = e^{-(K_1A_1 + K_2A_2)(t/V)} \tag{4}$$

where the subscript 1 refers to the Lucite surface itself, and the subscript 2 refers to the material being tested. The values of K_1 were determined by experiments with the chamber empty. We wish to note that the stirred-tank model was also used by Turk (1963) in his investigations of models suitable for describing the transient concentrations of odors within enclosures.

Predicted Indoor vs. Outdoor Concentrations of Ozone

We present some idealized solutions to the model equation to obtain qualitative information regarding indoor concentrations of ozone.

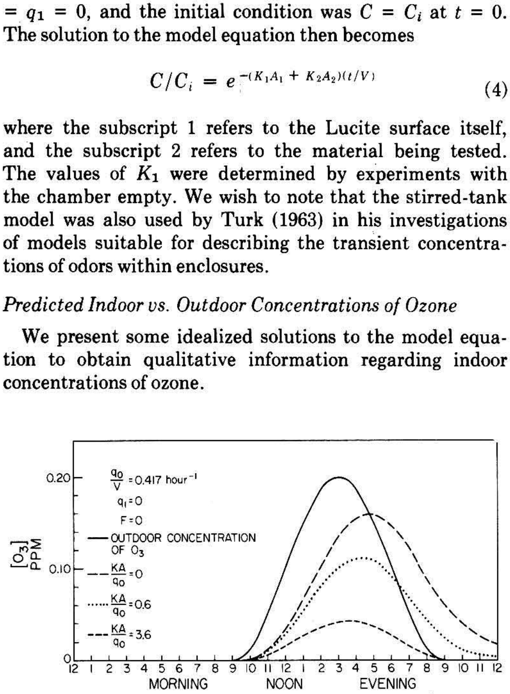

Figure 12. Calculated ozone concentration vs. time for a typical building without ventilation: Infiltration only

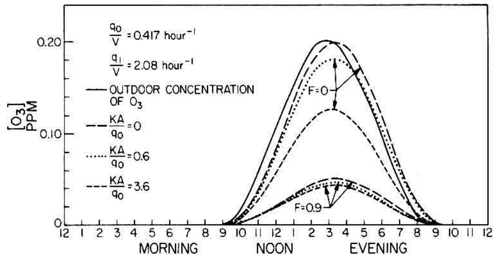

Figure 13. Calculated ozone concentration vs. time for a typical building with ventilation: Influence of filters

Calculations were performed for a dwelling having values of $q_0/V = 0.416$ hr^{-1}, no ozone source, and no internal recirculation of indoor air either through the central ventilation system or through an auxiliary system. The outdoor concentration of ozone was considered to vary sinusoidally during a 12-hr period starting from zero at 9:00 a.m., rising to a maximum of 0.2 ppm at 2:00 p.m., falling to zero at 9:00 p.m. and remaining at zero until the next morning at 9:00 a.m.

In case 1, the ventilation rate is zero, and thus the only air flow through the building is due to infiltration. In Figure 12, the solid line represents the outside concentration of ozone; the broken lines represent the calculated indoor concentration of ozone for various values of ΣK_jA_j. In this case the peak indoor concentration of O_3 should occur earlier, and be of lower value, with increasing value of ΣK_jA_j. This calculation also suggests that typical infiltration rates (Tamura and Wilson, 1963) are high enough to suggest the use of filters effective in destroying ozone. Note the qualitative similarity between Figure 12 and Figures 2 and 3.

In case 2, the ventilation rate is such that $q_1/V = 2.08$ hr^{-1} as shown in Figure 13, the broken curves with maxima above 0.1 ppm are associated with a value of $F = 0$ (i.e., no or ineffective filter with respect to ozone). The broken curves with maxima around 0.05 ppm are associated with a value of $F = 0.9$. This calculation suggests that use of filters can be an extremely effective way to greatly reduce the indoor concentrations of ozone.

Summary and Conclusions

In many instances the ozone concentration inside buildings is undesirably high, but it can be reduced to acceptable levels by rather simple means. The specific findings may be listed as follows:

Residence times associated with typically well ventilated buildings are generally not long enough to allow indoor ozone levels to become much lower than those outside.

The ozone level within homes decreases at rather rapid rates, once the doors and windows are closed.

The rate of ozone decomposition within buildings is first order with respect to the ozone concentration.

Decay rate constants for several common surfaces ranged in value from about 10^{-1}–10^{-3} ft^3/ft^2-min. Materials such as rubber, fabrics, and plastics have rate constants higher than metals and glass.

The mechanism of ozone decomposition within buildings is heterogeneous, and the rates depend directly on the surface-to-volume ratio.

All materials tested demonstrated an "aging" process defined as a substantial decrease in the rate constant over an extended period of exposure to ozone.

One material, plywood, appeared to have reversed the "aging" process after remaining in an ozone-free atmosphere for two days.

Certain commercially available filters can be extremely effective in lowering current indoor concentrations of ozone. Activated charcoal is an excellent filter for this purpose.

A stirred-tank ventilation model, involving first-order heterogeneous reactions, predicts ozone concentrations vs. time profiles which are similar to those measured.

Acknowledgment

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New Association for Aerosol Research Founded

A new scientific association for aerosol research was founded on October 18, 1972, in Frankfurt a.M., Germany. Purpose of the Gesellschaft für Aerosolforschung (GAF) is to advance all fields of aerosol research in science and technology. With the growing importance of aerosols in various disciplines like biology, medicine, chemistry, physics, technology, meteorology, hygiene, and many others, the new association will serve to bring scientists of all aspects of aerosol research together and to provide means of contact for all people in the scientific and technical community who have an interest in aerosol problems. GAF will make a particular effort to advance the interdisciplinary cooperation in aerosol research. The new association will operate on an international level. Presently, GAF has members in several countries, including Austria, France, and the United States.

A board was elected at the founding session. The members agreed to give priority to an effort to continue and to extend an annual meeting on airborne matter which had been held in Frankfurt and Mainz in the past.

Professor Dr. Böhlau, Frankfurt/Bad Soden, was elected chairman of the board and Professor Dr. Straubel will serve as secretary general. Inquiries may be directed to:

Gesellschaft für Aerosolforschung
6232 Bad Soden bei Frankfurt/Main
Rossertstrasse 11
Germany (Telephone: 06196-27051)

Iron–Phosphate Compound Identification in Sewage Sludge Residue

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■ The iron phosphate compound, vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$], has been identified by use of X-ray powder diffraction techniques, as existing in the dried secondary sludge residue of the Milwaukee Jones Island sewage treatment plant. In identifying this compound, various methods of drying the sludge residue were evaluated. Magnetic separation techniques were used to concentrate and separate vivianite from the bulk of the dried material. Analysis indicated that vivianite existed in a concentration of about 1 wt % of the dried material.

It is often desirable, when analyzing the performance of a sewage plant, to identify various crystalline compounds being formed in the sludge residues. Powder X-ray diffraction techniques can be used to fulfill this objective if the compounds being identified are crystalline and in a concentration in excess of approximately 10%. Unfortunately, compounds of interest, such as phosphates, tend to be in trace concentrations in the combined sludge, which makes their identification difficult by any means of analysis (Jenkins and Menar, 1967). If a means could be devised to concentrate the species of interest, then powder X-ray diffraction methods could be used to quantitatively identify these species.

It was initially suspected that a degree of phosphate removal was occurring in the Milwaukee Jones Island Sewage Plant via the formation of iron phosphate compounds (Leary et al., 1972). If this were true, then these compounds might be magnetic in nature, and magnetic separation techniques could be used to concentrate and segregate the species to be identified.

Results and Discussion

Samples of sludge residue were obtained from the Milwaukee Jones Island sewage treatment plant in the form of a secondary sludge. A volume of ⅓ to 1 gallon of sludge was processed for each analysis to obtain a powder that could be analyzed via X-ray diffraction techniques.

The sludge was first centrifuged, using an International Model CS Centrifuge, to remove the bulk of the liquid. The concentrated sludge was then dried using one of three methods. In the first method, the concentrated sludge was heated to 103°C to drive off the remaining water. It was felt that this method of drying could result in chemical reactions occurring in the sludge residue beyond those which had originally occurred in the sewage treatment plant and, thus, any chemical analysis would not be representative of the true nature of the sludge residue. For this reason, this method of drying was subsequently abandoned. The second method of drying consisted of drying the centrifuged material in air at room temperature. This drying process led to a hard granular material having particles up to a millimeter in size. Freeze-drying was the third method explored. In this method the centrifuged sludge was dried in a Virtis Model 10-010 Automatic Freeze Dryer. The freeze-dried material was fibrous in character, with particles dispersed within the fibrous matrix.

Specimens for X-ray diffraction analysis were formed by grinding the dried material to a powder and loading it into 0.5-mm-diam glass capillaries. These capillaries were mounted in a 114.6-mm-diam Phillips powder diffraction camera. The specimens were then exposed to a beam of X-radiation, obtained from an iron X-ray tube, for periods from 2 to 6 hr. Iron radiation was chosen to minimize the fluorescent radiation which might result from iron compounds. Identification of the unknown crystalline species was accomplished by comparing the observed powder diffraction pattern, after correcting for film shrinkage, with ASTM files (Cullity, 1956).

In the initial studies, specimens for X-ray analysis were obtained by selecting a random portion of dried sludge from each of the drying processes. The resulting X-ray diffraction patterns were found to be quite complex in that they exhibited a large number of diffraction lines with a high degree of background darkening. This indicated that a wide variety of crystalline and amorphous compound species existed in the sludge residue. The complexity of these patterns suggested that the crystalline compound species to be identified would need to be separated and concentrated if X-ray diffraction analysis techniques were to be successful.

It was known that when iron, in the form of waste pickle liquor, was added to the Milwaukee Sewage Commission's east plant an enhancement in the concentration of phosphorus in the sludge residue resulted (Leary et al., 1972). This indicated that an iron–phosphate compound

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[1] To whom correspondence should be addressed.

might be responsible for a portion of the phosphate removal. It was thus reasoned that magnetic separation techniques might aid in separating and concentrating this species such that it could be identified. This was found to be the case when the dried residue was ground to a fine powder and dropped between the pole faces of a 10-kG electromagnet. A sketch of the experimental apparatus used for the magnetic separation is shown in Figure 1. Several procedural steps were followed when magnetic separation was used. The total amount of powdered material was weighed. The powdered material was then dropped between the pole faces of the electromagnet until no further material could be magnetically separated from the bulk sample. The magnetically separated material was also dropped between the pole faces several times in an attempt to rid the specimens of as much nonmagnetic material as possible. Finally, the magnetically separated material was weighed.

Specimens as described in Table I were investigated using X-ray diffraction methods. The weight percent of the dried sludge which was magnetically separated from the various specimens is shown in Table II. The results of the X-ray powder diffraction studies are given in Table III.

The first columns of Table III contain the *d*-spacings and relative line intensities from the ASTM files for the inorganic crystalline compound, vivianite: $Fe_3(PO_4)_2 \cdot 8H_2O$. Specimens of vivianite obtained from a commercial supplier, designated as specimen C, led to a similar pattern as this standard. Specimen C was selected from large brown to black single crystals of vivianite. These crystals were found to be magnetic.

Specimen FD-E-1, as is noted in Table I, was obtained by selecting small brown to black crystalline particles from the magnetic material that had been separated from the East Jones Island plant freeze-dried sludge. The X-ray powder pattern for this specimen also agrees in an excellent manner with the ASTM standard pattern for vivianite. This result is in agreement with the results reported by Dow Chemical Co. (Wukasch, 1968).

The results of X-ray analysis for specimens FD-E-2, FD-W-3, AD-E-1, and AD-W-2, upon first inspection, do not seem to fit the standard pattern for vivianite as well as might be desired. However, upon further consideration these results are as should be expected. It should be noted that specimen FD-E-1 was composed of crystals selected from the magnetically separated material which had not been ground. The latter four specimens were obtained from magnetically separated powdered material. Therefore, the presence of trace amounts of other species is possible and would account for the trace lines in the X-ray patterns. It was also observed that certain lines were missing and that the relative intensities of the lines present were not in exact agreement with those of the standard. This, again, can be rationalized if the nature of the specimens is taken into account. Vivianite has been proposed to exist in a defect form ("oxidized vivianite") as a result of the oxidation of a portion of the ferrous iron to ferric iron, which would lead to a more diffuse X-ray pattern (Palache et al., 1951). The line positions, or *d*-spacings, in the X-ray powder pattern would be nearly those encountered for the perfect crystalline structure, whereas, it is possible that the X-ray structure factors, which relate to the intensity of each individual line, could change dramatically (Mohanty and Azaroff, 1961). The intensity variations, of which missing lines are a part, as compared to the standard might be rationalized on this basis. From inspection of the results of Table III, it is observed that freeze-drying leads to patterns which compare more favor-

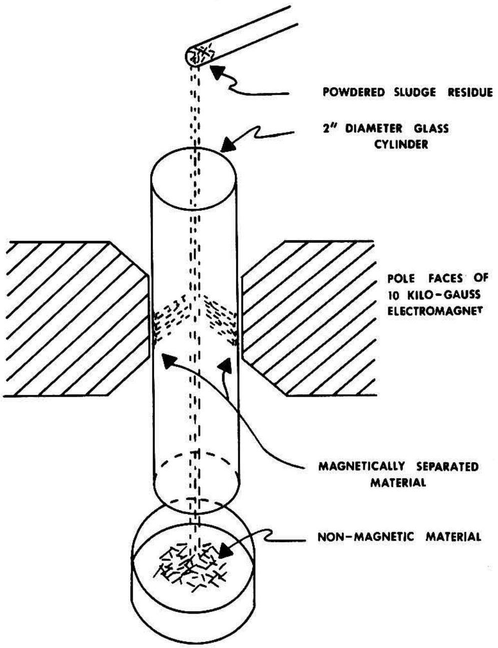

Figure 1. Apparatus used to magnetically separate sludge residue

Table I. Specimens Investigated in X-Ray Powder Diffraction Studies

Specimen[a]	
C	Crystalline sample selected from vivianite that had been obtained from a commercial source. This material was magnetic
FD-E-1	Group of black crystals selected from freeze-dried and magnetically separated sludge residue, obtained from the East sewage plant at Milwaukee
FD-E-2	Obtained from East plant sludge residue that had been freeze-dried, ground into a fine powder, and magnetically separated from the bulk material
FD-W-3	Obtained from West plant sludge which was treated in the same manner as specimen FD-2
AD-E-1	Obtained from East plant sludge residue that had been air-dried at room temperature, ground to a fine powder, and magnetically separated from the bulk material
AD-W-2	Obtained from West plant sludge which was treated in the same manner as specimen AD-1

[a] Upon being ground, the freeze-dried material led to a fluffy powder, while the air-dried material yielded a granular powder

Table II. Results of Weight Analysis on Magnetically Separated Powder

Specimen	Total powder wt grams	Wt of magnetic material, grams	Wt % of magnetic material
FD-E-2	29.9	1.19	3.98
FD-W-3	29.3	1.276	4.35
AD-E-1	13.2	0.193	1.46
AD-W-2	11.28	0.119	1.06

ably with the standard pattern, whereas air-drying leads to less desirable results. Freeze-drying would be expected to result in a lower rate of oxidation upon drying than the higher temperature air-drying technique.

Electron microprobe analyses were performed on the various specimens described in Table I. The results of these analyses indicated that iron and phosphorus were indeed major constituents in these specimens. Lesser concentrations of Si and Ca, and trace concentrations of K, Ti, Cr, Zn, and Cl were also observed. These results were somewhat qualitative due to the difficulty of various interferences and of setting up proper standards, but they tend to confirm the previous X-ray diffraction identification of vivianite.

Initial weight analysis studies, as shown in Table II, also deserve some comment. The results of these studies were strongly influenced by the texture of the powdered materials which were magnetically separated. The freeze-dried material was fibrous in texture, while the air-dried material was in the form of hard millimeter-sized particles. Upon grinding, it was found that the freeze-dried material resulted in a fluffy powder which had a tendency to pick up electrostatic charge, while the air-dried material gave a granular powder which did not become electrostatically charged. The higher weight percent of magnetic substance from the freeze-dry process seems to be due to the fact that some of this material was electrostatically attracted to the wall of the glass cylinder as is shown in Figure 1. It is felt that the weight analyses of the air-dried samples are more reliable at this time. These were in better agreement with the results that were expected for the East plant where waste pickle liquor containing iron was added, as compared to the West plant, where no additions were made (Leary et al., 1972).

It should be pointed out that other crystalline compound species that have not been isolated or identified exist in the bulk of the nonmagnetic sludge residue. Other techniques of separating and concentrating these species will be required before they can be identified.

Summary of Results

Lower temperature freeze- and air-drying methods which limit chemical reactions beyond those occurring in the sewage treatment plant are better than the higher temperature drying process for reducing the sludge residue to a powdered form for X-ray analysis. To use the X-ray powder diffraction technique to identify compound species in sludge residues, it was found that the species must be concentrated and separated from the bulk material. Vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, was observed to be magnetic and was separated using magnetic separation techniques. Vivianite in a defected form was found to be present in the sludge residue of the Milwaukee sewage treatment plants in a concentration of about 1 wt % of the dried sludge. The freeze-drying method led to better results upon X-ray analysis, while room temperature air-drying seemed to yield a more reliable weight analysis.

Acknowledgment

The efforts in the initial portion of this study of Louis Cartz, Elluru Gopalakishna, Srinivasan Natarajan, and James Winters are greatly appreciated.

Table III. Results of X-ray Analyses of Specimens Investigated[a]

Vivianite (ASTM Card 3-0070)		C		FD-E-1		FD-E-2		FD-W-3		AD-E-1		AD-W-2	
d, Å	I/I_o, %	*d*, Å	I/I_o	*d*, Å	I/I_o	*d*, Å	I/I_o	*d*, Å	I/I_o	*d*, Å	I/I_o	*d*, Å	I/I_o
		8.72	T			8.86	T	8.62	M				
						8.43	T			8.56	T		
8.00	27	7.93	M	7.98	M								
		7.38	T					7.42	VS	7.25	VS	7.23	VS
6.80	100	6.80	VS	6.69	VS	6.83	VS	6.92	VS	6.90	VS	6.90	VS
		5.40	T										
4.91	40	4.91	M	4.88	M	4.92	W						
4.50	13	4.57	T	4.55	W								
4.32	4	4.37	T										
4.09	13	4.08	W	4.06	W	4.09	W	4.09	S	4.05	M	4.08	S
3.84	40	3.85	M	3.84	M	3.87	W						
3.65	5	3.66	T										
		3.55	T										
3.33	3	3.34	T	3.34	W	3.35	T	3.34	S	3.35	M	3.34	M
3.20	53	3.22	M	3.20	M			3.21	T				
		3.00	M									3.05	M
2.97	67	2.97	W	2.97	S	2.97	M	3.04	W	3.03	T	2.87	W
2.71	67	2.74	M	2.71	M			2.81	T	2.88	W		
2.64	8	2.64	W					2.60	T				
2.52	33	2.53	M	2.52	M	2.53	VS	2.48	W	2.52	T	2.53	M
2.42	40	2.43	M	2.42	W								
2.31	27	2.32	M									2.29	T
		2.28	T										
2.23	20	2.24	W										
2.19	20	2.20	W										
2.07	23	2.08	W			2.09	W						
2.01	8	2.02	T			2.03	W						

[a] Symbols representing the intensities, I/I_o, of the various diffraction lines are: VS, very strong; S, strong; M, medium; W, weak, and T, trace. Filtered iron radiation and a 114.6 mm-diam Phillips Powder Diffraction Camera were used. Corrections were made for film shrinkage and the camera was calibrated periodically using silicon as a standard.

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Heavy Metals: Fallout Around a Power Plant

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■ Soils around a coal-burning plant are enriched in Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti, and Zn. Plant materials are enriched in Cd, Fe, Ni, and Zn. Soil enrichments correlate with wind patterns and with the metal content of coal except for Hg, which is only slightly enriched.

Airborne mercury resulting from fossil fuel consumption is frequently cited as a source of mercury in isolated lakes. Studies by Joensuu (1971) and Billings and Matson (1972) suggest that large quantities of mercury may enter the environment in this way. Bertine and Goldberg (1971) consider fossil fuel consumption to be a potentially significant source of atmospheric discharge of many metals in addition to mercury. The research reported in this paper was set up to gain an entry to this problem of atmospheric discharge, specifically, to consider how much land area might be burdened by fallout from a major coal burner.

Study Area

The plant is located on the eastern shore of Lake Michigan. Except for a ridge of low dunes at the shoreline, the surrounding terrain is quite flat. Typically, the soil is sand with a thin cover of decomposed organic matter. The closest potentially competing source of atmospheric discharge of metals is the city of Holland, lying six miles to the south, which has several metal industries. The plant was started up in 1962. Since then it has consumed about 10^7 tons of Ohio coal. It presently generates 650 MW, and discharges through a 400-ft stack equipped with precipitators which operate at about 90% efficiency.

Sampling and Analysis

The land sampling grid included 45 sites, with two samples taken at each site. Usually, samples were soils from established wooded areas, one from under deciduous trees, the other from under coniferous trees. All samples were taken from well-drained areas. The samples were 2 cm thick, and were screened to remove leaves, roots, pebbles, etc. An additional 24 surface grabs were taken of sediments in Lake Michigan, up to 3 miles offshore.

The samples were analyzed as received, and the results corrected to a dry weight basis. Two-gram samples were weighed into screw-top centrifuge tubes, and initially oxidized at room temperature in an H_2SO_4–$KMnO_4$ medium. When the $KMnO_4$ oxidation appeared complete, 2 ml. of 4% $K_2S_2O_8$ was added and the tubes were sealed and placed in a 60°C oven for 30 min. The samples were then centrifuged, and the supernatant was decanted and brought to volume. Mercury analysis was done by flameless atomic absorption, using the Mercometer (Anti-Pollution Technology Corp.). Conventional AA analyses for Fe, Ti, Zn, Co, Cr, Cu, Ni, Cd, and Ag were run on Perkin-Elmer 303.

Results and Discussion

The analytical results, plotted as contour maps, are all quite similar to that of Cr (Figure 1). All patterns show marked enrichment northeast and southeast of the plant, with a pinched-in area of low concentration at about 80°. Enrichment patterns in the sediments do not coincide well with the land patterns, being complicated by the outward movement of fine particles resulting from wave action, by the general southward drift of near-shore sediments in this area, and by significant river discharge of metals. The Hg pattern differs from the others in that it lacks the region of very low concentration around and south of the plant.

To gain some insight into the possible entry of the discharged metals into the biota, samples of native grasses, maple leaves, and pine needles from four sites in the background region and four sites in the enriched region were collected and analyzed. The data (Table I) show highly significant increases in Cd, Fe, and Ni. Thus, cattle pastured in the enriched region are ingesting grasses with a considerably greater Cd content than cattle pastured in the background region.

The wind data presented in Figure 2 are the summary of 3-hr observations over four years at the U.S. Weather Bureau station at Muskegon, 18 miles north, and near the shoreline. The most frequent wind component is 13–18 mph. The pattern has been rotated 180° from the conventional wind rose, to better illustrate a resulting fallout pattern. The wind pattern is quite similar to the observed fallout patterns, with winds of maximum frequency directed northeast and southeast of the plant, relatively low frequency directed at about 80°, and a very low frequency of low-velocity winds. The main difference between the wind pattern and the fallout patterns is that the observed southern enriched zone is too large east to west. Possibly this is the result of the airborne debris of the city of Holland, reinforcing the pattern from the plant. The northeastern enriched region is centered about 6 miles from the plant; thus it appears that 13–18 mph winds are competent to transport the particulate emissions about 6 miles. The wind pattern shown has been empirically scaled accordingly; that is, a wind velocity vector of 15.5 mph corresponds to a map distance of 6 miles.

If the wind pattern, as scaled, adequately explains the observed fallout patterns, then it appears from the wind pattern that about one fifth of the discharge from the

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Table I. Trace Metals in Soils and Plant Materials around a Power Plant

Metal	Background soils, ppm	Enriched soils, ppm	Background plants, ppm	Enriched plants, ppm	Soil enrichment, tons	Total discharge, tons	Calcd discharge, tons
Fe	1500	2840	80	260	20,000	25,000	10,000
Ti	55.6	91.6	None detected		540	680	500
Zn	26.3	35.0	37	51	130	160	50
Co	2.3	4.6	None detected		34	42	5
Cr	4.6	6.5	None detected		28	35	10
Cu	2.8	4.6	10	8	26	32	15
Ni	2.4	4.0	0.5	2.1	24	30	15
Cd	0.55	1.46	0.12	0.35	14	18	
Ag	0.247	0.272	None detected		0.4	0.5	0.5
Hg	0.0079	0.0102	0.09	0.07	0.04	0.05	4

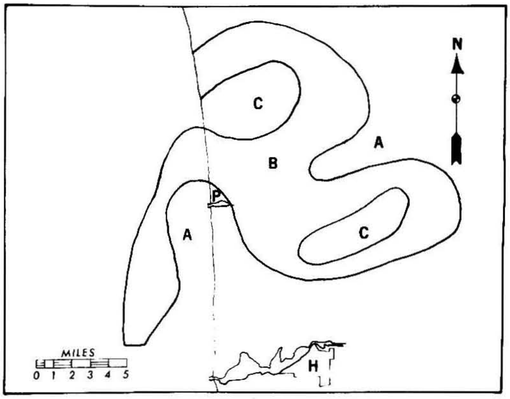

Figure 1. Chromium distribution around the power plant

P, plant; H, city of Holland; A, 0–5 ppm; B, 6–10 ppm; C, over 10 ppm

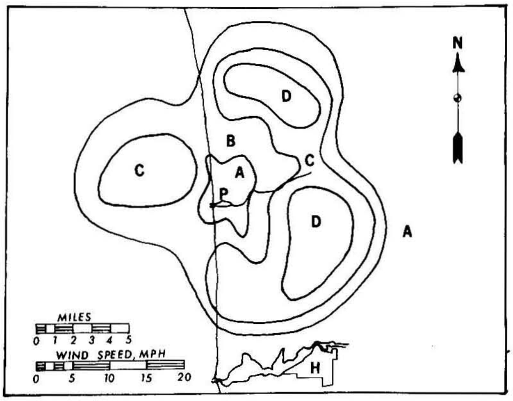

Figure 2. Wind distribution around the power plant

Total observations, 14,000; A, 0–125 observations; B, 126–250; C, 251–375; D, over 375.

plant enters Lake Michigan. As shown by Figure 1, however, this one fifth is not located where the wind pattern predicts, probably because of movement of sediments discussed previously.

By making the following assumptions, an approximate balance between coal consumption and the soil concentrations can be constructed:

- There is a single region enriched by coal burned at the plant. This region is shaped like the shaded land area of Figure 1. Outside this region the metals are at background concentration. The enriched area covers 115 mi^2 and encloses 23 of the 45 land sample sites.
- Enrichment is confined to the upper 2 cm of soil, which has a density of 2.7 gm/cm^3.
- Except for Hg, metal concentrations in the coal are those presented by Bertine and Goldberg (1971). The concentration of Hg is taken as 0.3 ppm, an estimate possibly in error by a factor of 5.
- The precipitator works with 90% efficiency for all metals but Hg. All the mercury in the coal is discharged to the atmosphere (Billings and Matson, 1972).

Each assumption may be in error by a factor of 2 or 3, but less than an order of magnitude. The assumptions permit calculation of an observed total discharge, in metric tons, and a calculated discharge based on an assumed coal analysis. The numbers are shown in Table I . The range from Fe to Ag covers nearly five orders of magnitude, and only Hg shows a serious discrepancy, by about two orders of magnitude.

There are several possible explanations for the discrepancy:

- The assumed mercury concentration in coals may be too high. To remove the discrepancy would require that the mercury concentration must be about 0.003 ppm, which is unreasonably low. This explanation is probably incorrect.
- Mercury leaves the stack as the vapor, adsorbs on the particulates and deposits with the other metals. Once in the soil most of it is volatilized from the particulates by some unknown chemical or biological process and dispersed over a wider area.
- Mercury leaves the stack as the vapor, a small fraction is adsorbed on particulates and deposits, and the balance is dispersed over a wide area.

Although we cannot distinguish between the latter two explanations, it is clear that mercury discharged to the atmosphere by combustion of coal is much more widely dispersed to the environment than are other metals similarly discharged.

Acknowledgments

We thank J. Brower, J. Monds, and W. Paplawsky for technical assistance and J. Reynolds of Consumers Power Co. for plant operating data.

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INDUSTRY TRENDS

Combustion Engineering will build a $16 million steam generating unit for Central Illinois Public Service Co. which will allow the utility to boost its electric generating capacity by some 30%. The 600-mw boiler will be fueled with midwestern bituminous coal and will be equipped with an overfire air system to reduce formation of NO_x.

Envirodyne Inc. has exercised its option to acquire Environmental Triple S Company (ETS) in exchange for Envirodyne common stock in an amount to be determined by future ETS earnings level. ETS was organized to provide process and services to monitor and control pollution. Envirodyne is an expanding environmental technology company that provides professional consulting services, pollution control products, and advanced R&D programs.

J. F. Pritchard & Co. will provide design, engineering, and procurement for a Grande Paroisse extended adsorption system for Mississippi Chemical Corp.'s Yazoo City fertilizer complex. The Grande Paroisse system is another step in Mississippi Chemical's emission control program which involves capital expenditures of more than $15 million.

Procon Inc. international engineering and construction company and subsidiary of UOP, has been awarded a contract to serve as engineering manager for La Societe Nationale Sonatrach in construction of a plant to liquefy 1.2 billion cfd of natural gas at Arzew in Algeria.

Westinghouse Electric Corp. has been awarded a contract by Northeast Utilities to provide a 1,150,000-kW nuclear steam supply system for the proposed Millstone Point generating station at Waterford, Conn. The unit is scheduled to begin operation in 1979. The contract brings to 84 the number of Westinghouse reactor systems in operation, under construction, or on order.

Hyon Products Co. division of International Hydronics Corp. will offer the Hyon "TU-WIN" process for treating electroplating rinse waters. Hyon will either sell or lease the "TU-WIN" process installation.

Andco Environmental Processes, Inc., is selling its water treatment system to Buckeye Steel Casting Co. of Columbus, Ohio, and Dresser Transportation Equipment Division, Dresser Industries, Inc., of Buffalo, N.Y. Two contracts represent first sales of the complete package plants by Andco.

BiO_2 Systems, Inc., has licensed Bio-Pure, Inc., Tualatin, Ore., to manufacture and sell its recently patented home aerobic sewage treatment units. Bio-Pure specializes in sewage and waste treatment equipment.

Rust Engineering Co. will engineer and construct an effluent treatment facility for the Chesapeake Corp. of Virginia at its pulp and paper mill in West Point, Va. The facility will cost about $5 million. Included is a primary clarifier, a cooling tower, secondary treatment to remove organic loading through the UNOX oxygenation system and two secondary clarifiers to remove biological sludge. Rust is also installing a 100-tpd onsite oxygen generating plant for the UNOX system.

Bethlehem Steel Corp. has been awarded a U.S. patent for a process to recover fine particles of coal from water in a coal-processing plant. The invention permits the used water to be recycled in the plant or fed to other ground or surface waters without danger of pollution.

Sippican Corp. and Le Messurier Associates, Inc., will form a new environmental engineering group with broad capabilities in building and environmental design. The establishment of the group has been accomplished by virtue of an agreement in principle whereby Sippican will acquire 80% of the outstanding capital stock of Le Messurier Associates, Inc.

Peabody Engineering will design, engineer, fabricate, install, and start up a turn-key ammonia-based SO_2 removal system for Conserv, Inc., a Lakeland, Fla., phosphate chemicals company. The system will use a Peabody impingement tray absorber to remove SO_2 and a Peabody/Lurgi radial scrubber to remove ammonia sulfate fines and other particulates. System is designed to handle tail gases with an SO_2 content of about 32,000 lb/day. System will be in operation by spring 1973.

Babcock & Wilcox has been awarded a $2.5 million contract to supply a chemical recovery boiler for British Columbia Forest Products, Ltd. (BCFP). The boiler will process 2,400,000 lb/hr of black liquor solids per day. Spent black liquor will be burned efficiently in the furnace and chemicals recovered for recycling to the pulping process. The unit will go on stream at BCFP's mill at Crofton on Vancouver Island, B.C., Canada.

Applied Biochemists, Inc., has received Patent No. 3,716,351 covering a method of preparing copper and triethanolamine in a stable formulation to be used in algaecides.

Battelle Pacific Northwest Laboratories will build a major environmental and life sciences laboratory at its Richland Research Complex. Estimated cost of the 100,000-ft.^{2} building and related construction is $5.7 million. Construction is expected to begin this month with completion date of September 1974.

FMC Corp. has purchased for an undisclosed amount all assets of the "Marox" pure oxygen treatment process developed by the Martin Marietta Corp. Among the Marox processing advantages, FMC says, is that the need for closed reactor tanks is eliminated, the process consumes less power, and has oxygen transfer efficiencies in excess of 95%.

Foster D. Snell, Inc. (Florham Park, N.J.), a wholly owned subsidiary of Booz, Allen & Hamilton, Inc., and Poly-Con Corp., have signed a joint marketing agreement to provide consulting services equipment, and systems for pollution control. Joint effort will emphasize effective liaison between regulatory agencies and clients with air pollution problems.

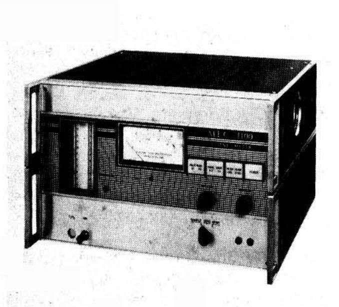
Penetryn International Inc. (Latham, N.Y.) has acquired PTT, Inc., a water-cooling tower manufacturer. Penetryn has renamed the company Delta Technology, Inc., and says that Delta will operate as a wholly owned subsidiary. Penetryn specializes primarily in water pollution control.

Aerojet General Corp. has purchased Chemical Construction Corp. (Chemico), a New York City-based subsidiary of Boise Cascade Corp., for an undisclosed amount of cash. Chemico had 1972 sales of about $70 million. Aerojet had sales of about $278 million with a net income of $13 million in the same period.

Joy Manufacturing Co. announced an agreement with Pennsylvania Power and Light Company of Allentown to install and operate a wet limestone scrubbing system pilot plant at PP&L's Sunbury Station. The pilot unit will clean 12,000 cfm gas using an integral electrostatic device which will eliminate liquid droplets from the gas-scrubbing equipment. Specialized slurry treatment will minimize limestone consumption. The pilot plant is scheduled to begin operation this spring.

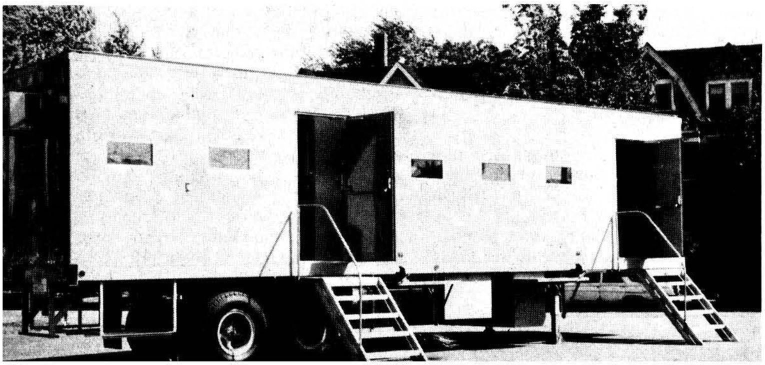
NEW PRODUCTS

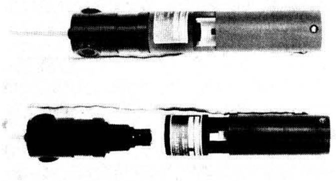
CO_2 alarm
New alarm system is designed to safeguard the contents of CO_2 chambers against loss of gas. Pressure is adjustable from 10–35 psi. When input pressure drops to preset danger level, the alarm provides a loud audible warning signal before the tank needs replacing. The compact size conserves valuable bench space. Lab-Line Instruments, Inc. 61



Ozone meter
New meter uses photometric detection of chemiluminescence resulting from flameless reaction of ethylene gas with ozone. Meter specifically detects ozone in presence of NO_2, SO_2, and other gases which normally interfere. Unit uses solid-state circuitry and has four push-button ranges covering 0–10.0 ppm. Available in bench or rack model. McMillian Electronics Corp. 62

Mobile lab
Van-type laboratory for air and water pollution monitoring is suitable for industrial or governmental application. Interior of semistyle laboratory is outfitted as a complete and modern laboratory with heating, lighting, utilities, sinks, fume hoods, and similar equipment. Unit can be completely self-sufficient since it carries its own sanitary water tank and disposal system. Heating and air conditioning are included. Calumet Coach Co. 63





Laboratory RO
Household or laboratory size complete reverse osmosis water treatment system reduces total dissolved solids by as much as 95% in up to 500 gpd of water. Solids removed include chlorides, sulfates, sodium, calcium, and other solids. Iron oxide and hydrogen sulfide can be removed if needed. Puredesal, Inc. 64

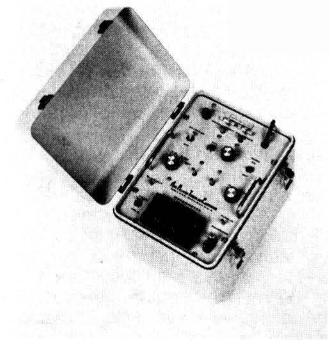
Environmental chamber
New series of 65-ft^3 temperature-humidity test chambers offers flexibility as well as simplicity of operation. Chambers have a standard temperature range from 0–200°F, complementing the humidity range of 20–95%. Tenney Engineering, Inc. 65

Filters
Porous block filter bottoms can be used in water-purification systems. Modular units are designed to provide higher strength with lower installation and replacement costs than are provided by plate bottom filters. New filters are used to support rapid sand filters or activated carbon adsorption units for water or waste water treatment. Units come in standard 2-ft by 1-ft modules consisting of fused alumina porous plate bonded to a clay saddle. Special sizes and shapes are available. Norton Co. 66

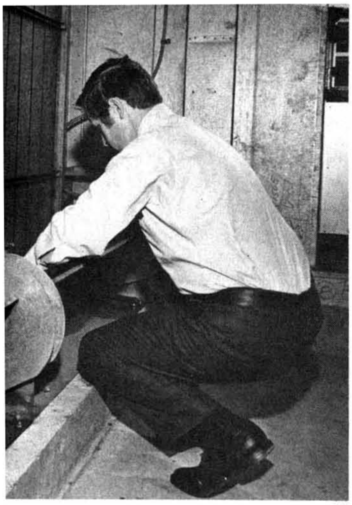
Air compressor
Portable air compressor silenced in very low cfm range is a sound-insulated version of small but powerful compressors available for some time. The 85-cfm unit is designed for use in environments such as schools, hospitals, and private residences where noise must be controlled. At 1 meter, the unit operates on load at 85 dB. Atlas Corco 67

D.O. probe
New foul-proof probe and agitator assembly for continuous monitoring and control of dissolved oxygen permits unattended measurement of oxygen in waste stream treatment systems, ponds, streams, etc. Probe features include automatic compensation for pressure and temperature changes, easy screw-on cap for membrane replacement, and glandless, paddle-action agitator which cannot be clogged by waste material. Delta Scientific Corp. 68

Conductivity meter
Low-cost Type 70 conductivity meter measures five ranges from 0–20,000 micromhos/cm. Features 6-in. meter printed with five scales. Unit is completely portable, powered by mercury batteries. Solid-state circuitry is stable and easily serviced. Dip-type probe automatically temperature-compensated is included with the meter. Chemtrix, Inc. 69



Mercury detector
Battery-powered digital readout portable AA spectrophotometer measures mercury vapors. Instrument contains built-in transistorized air sampling pump with capacity of about 1.5 l./m when used with gas washing bottle. Unit is drift-free while operating over long periods of time since total power consumed is less than 30 W when operated from a power line (less than 12 W from battery). Anti-Pollution Technology, Corp. 70



Roll filter replacements
Prime manufactured fiber glass air filter media are factory-mounted on precise cores to fit many popular machines without modification. DRiCO Industrial Corp. **71**

Heat flux sensor
Heat flux transducer can be lowered in drilled core to sense potential of geothermal power. Output of transducer is typically 2 ml for each Geothermal Flux Unit, or 10^{-6} cal/sec cm^2. Thermonetics Corp. **72**

Humidity/temperature indicator
Light-weight compact versatile lab and field instrument consists of naturally aspirated probe which contains both the sensors and a control housing with solid-state electronics. Unit has single-scale readout for both relative humidity (0–100%), and temperature (0–100°F). Humidity sensor is a hygromechanical arch which bends as humidity varies and actuates strain gages in a bridge circuit to produce dc voltage output. Meteorology Research, Inc. **73**

Oxygen analyzer
Fast response paramagnetic oxygen analyzer is a low-cost instrument for continuous measurement of oxygen ranging from 0–25% concentration. Analyzer features linear output, excellent stability, and overall response time of 2 sec. Built-in flowmeter provides accurate metering of sample gas. Scott Research Laboratories, Inc. **74**

Recorder
Unit is 3-pen recorder with all pens overlapping and writing the full 10-in. chart width. Has an 11-step attenuator input from 1 mV to 20 V, 24 chart speeds, 200% zero adjust, potentiometric to 200 mV and Mohm on higher ranges. Uses Z-fold or rolled paper. Soltec Corp. **75**

Sample preparation
Asbestos fibers and toxic metals from blood and tissues can be retrieved with Plasmod. Unit takes advantage of plasma chemistry technique which eliminates high temperatures or wet chemicals in preparation of inorganic ash for laboratory analysis. Ionized gas causes a gentle, low-temperature combustion of organics in the specimen leaving inorganic trace metals or other residue for analysis. Combustion products are carried away in the gas stream. Duke Science Corp. **76**

Sound absorber
High-performance, sound-absorbing polyurethane foam is reticulated material which combines good acoustical characteristics, flame retardance, abrasion resistance, and esthetic qualities of a patterned, cleanable surface. Foam is particularly effective in the 250–630 Hz low-frequency range where reciprocating or rotating equipment often causes noise problems. Scott Foam Div. **77**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

NEW LITERATURE

Water temperature. Bulletin describes temperature recording accessory for use with Stevens Type A Recorder. Sensor can be placed in water or other liquid up to 100 ft from recorder. Leupold & Stevens, Inc. **91**

Sludge press. New brochure describing sludge press capable of raising sludge consistencies from 3% to as much as 50% in one operation. Brochure describes unique twin-roll unit which automatically compensates for feed rate, freeness, and consistency to dewater organic sludge to constant cake dryness. Ingersoll-Rand Environmental Div. **92**

Exhaust purifier. Bulletin announces availability of OC-50 exhaust purifiers for propane-fueled lift-truck engines. Bulletin also contains information on other exhaust purifiers for engines powered by leaded, low-lead or white gasoline, or diesel fuel. Oxy-Catalyst, Inc. **93**

Engineering services. New 7-part package entitled "Mission Possible" describes engineering capabilities and services and gives full particulars and background of engineering staff. Company specializes in engineered systems for chemical processing and pollution control, with emphasis on distillation and extraction. Chem-Pro Equipment Corp. **94**

Diffraction pattern. Brochure describes diffraction pattern sampling techniques and application. Technique uses laser-lens combination to perform sophisticated Fourier transform computation. Applications include precision measurements, pollution monitoring, particle analysis, image analysis, flaw detection, and automatic inspection systems. Recognition Systems, Inc. **95**

Waste water clarifier. Bulletin describes compact single, advanced water treatment system for pollution abatement. Simultaneously removes both floatable and settleable pollutants in about $\frac{1}{4}$ the retention time of the conventional dissolved gas flotation unit and $\frac{1}{122}$ of the retention time of settling tanks. Rheem Superior, Div. of Rheem Mfg. Co. **96**

Fish stupifier. Highly concentrated, liquid chemical stupifies fish and is nontoxic to man or other marine organisms. Allows collection of marine specimens without polluting the water with long-lived chemicals. Blue Spruce Co. **97**

Process control. Brochure presents latest pneumatic instruments for process control which includes remote mounted controllers and panel-mounted units designed for use in centralized control rooms. The Foxboro Co. **98**

Catalog. New catalog describes Teflon glass laboratory ware joints designed to replace standard taper ground glass joints. Glaseal Products **99**

Filtration. Bulletin illustrates line of cartridge filters, rotary vacuum filters, filter plates and frames, filter cartridges, automatic filter stations, high-volume filters, and temperature-resistant fabrics. Technical Fabricators, Inc. **100**

Environmental services. Brochure lists consulting services of company including water quality data collection programs, environmental systems analysis, and alternative methods of sewage disposal. Enviroquality **101**

Control valves. Bulletin briefly describes and illustrates product offerings in field of automatic control valves and accessories for the process industries. ITT-Hammel Dahl/Conoflow **102**

NO_x monitor. Bulletin details operating features of stack/vehicular chemiluminescent NO-NO_x monitor. Same bulletin includes information of atmospheric ozone monitor. REM Scientific, Inc. **103**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

Sampler. Bulletin describes portable liquid sampler with wide versatility. Capacity ranges from 10 to 2000 cm^3/min. The Clarkson Co. **104**

Data sheet. Data sheet describes high-speed laboratory rotor mill for discrete and continuous grinding of solid wastes, garbage, landfill, sewage, etc. Mill grinds to micron-size particles without the use of Dry Ice or liquid nitrogen. Geoscience Instruments Inc. **105**

Services. Brochure details capabilities of company which include consultation, collection and analysis, data reduction and interpretation, and recommendations for abatement or control programs. Environmental Research Group, Inc. **106**

Instrument line. Brochure explains firm's complete product line of pollution control and analysis, process control instruments. Great Lakes Instrument Co. **107**

Sodium bicarbonate markets. Illustrated brochure tells industry's myriad uses of sodium. Brochure contains wealth of data on properties and uses which could suggest additional ways for improving existing products. Church & Dwight Co., Inc. **108**

Personnel training. Total package approach to power plant personnel training outlined in new brochure. Company's approach provides integrated on-site training center housing classrooms, one or more simulated control rooms, video tapes and audiovisual equipment, self-teaching equipment and, optionally, a training reactor. NUS Corp. **109**

Air filtration. Booklet discusses elements to be considered in choosing an appropriate air filtration unit and provides data to aid in selection of proper fabric for collecting various kinds of effluent dust. Brochure covers properties of high-temperature-resistant nylon applicable to air-filtration market. Du Pont Co. **110**

Scrubbers. New two-color brochure covers line of Venturi, tray- and spray-cyclonic scrubbers. Includes flow diagrams of typical installations and applications to air pollution control in various fields. Swemco Inc. **111**

Environmental control systems. Information folder on environmental control systems contains various pieces of literature pertaining to Johns-Manville products, systems, and services designed to help control air and water pollution. Folder contains directory to company's environmental engineering department. Johns-Manville Inc. **112**

Chemical handbook. Two-hundred-page handbook of chemicals gives molecular formula, molecular weight, and important physical properties for over 100 lipids, pesticides, amino acids, carbohydrates, hydrocarbons, amphetamines, barbiturates and other chemicals of biological interest. Supelco, Inc. **113**

Polymers. Technical literature describes use of Hercules CMC and Natrosol hydroxyethyl cellulose to provide rheology and water retention in pigmented latex coatings for paper and paperboard. Literature includes six-page reprint from most recent issue of the "Hercules Chemist" discussing broad aspects of research program to determine effectiveness of polymers in paper coating. Hercules, Inc. **114**

Cooling tower control. Illustrated full-color bulletin tells of systems for automatically controlling chemical treatment of cooling tower water to keep tower free from scale and corrosion and provide a fail-safe backup function. Engineered control system eliminates haphazard manual control, time-consuming corrections, inadequate bleed-off, overaccumulation of solids, and overtreatment of recirculating water. Metropolitan Refining Co., Inc. **115**

Standards publication. First issue of "Duke Standards Chronicle" is 4-page periodical devoted to the subject of calibration and reference standards available to laboratories. First issue features asbestos fiber standards, surface area standards, and fine particle standards, among others. Duke Standards Co. **116**

Biodegradable plastics. Series of independent test reports on biodegradable plastics is available from company. Bio-Degradable Plastics, Inc. **117**

Data package. Data package on continuous-duty monitors and controllers for pH and ORP contains application drawings, engineering data, technical and dimensional specifications, installation drawings, and details of foul-proof probe. Data package is particularly useful to consultants and engineers. Delta Scientific Corp. **118**

Consulting services. Illustrated brochure outlines the company's operations consulting package for sewage treatment and water supply systems. Services include predesign consultation, system start-up, on-site inspection and supervision, operations personnel training, and emergency situation assistance. Gilbert Associates, Inc. **119**

Phosphorus removal. Technical bulletin tells how company's unit removes phosphorus in effort to reverse eutrophication of Shagawa Lake, Minn. Graver Water Conditioning Co., Ecodyne Corp. **120**

IR analyzer. Model 864 IR Analyzer is designed for wide range of process applications in gaseous or liquid streams. Specks of instrument are given in four-page publication which includes application data, photographs, and outline drawings. Beckman Instruments, Inc. **121**

Pumps. New catalog covers complete range of pumps manufactured or distributed by instrument company including centrifugal pumps, diaphragm-type air pumps, positive displacement, magnetic drive, immersion, metering, oscillating, positive pressure, gear type, self-priming, and explosion-proof pumps. Also describes multichannel cassette pump in various tubings. Cole-Parmer Instrument Co. **122**

C_3/C_4 sweetners. Technical brochure describes successful application of molecular sieve adsorbents for sweetening propane and butane from sour-gas feeds. Report summarizes 11 years' experience at three sour-gas treating plants in Canada which produce sales gas, sulfur, and condensate in addition to the sweetened C_3/C_4 fractions. Union Carbide Corp. **123**

Design. Company has published compendium called "Useful Information on the Design of Plate Structures," detailing applications of steel plates to various engineering problems. Provides good basic background on many facets of plate design. American Iron & Steel Institute, 201 East 42nd St., New York, N.Y. 10017 (Write direct)

Film. New 17-min 16-mm color sound film entitled "Earth's Human Shores" describes contamination of waterways by increased industrial effluents and domestic sewage. Focuses on Zimpro's sludge disposal method. Modern Talking Picture Service, 2323 New Hyde Park Road, New Hyde Park, N.Y. 10040. (Write direct.)

BOOKS

Management and Engineering Guide to Economic Pollution Control: A General Approach to Industrial Waste Problems With Case Histories. David Krofchak. 124 pages. Clinton Industries, Inc., Publishing Div., P.O. Box 1208, 32880 Dequindre Ave., Warren, Mich. 48092. 1972. $10, paper.

Attempts to describe the fundamentals of an economic approach to the solution of difficult industrial waste treatment problems. Illustrates how management can turn seemingly money-losing pollution abatement programs into cost-saving improvements to production processes. Also reference source for engineers.

Vibration and Noise in Motor Vehicles. viii + 207 pages. The Institution of Mechanical Engineers, 1 Birdcage Walk, London SW1 9JJ, England. 1972. £ 6.50, hard cover.

Written for engineers, researchers, and academicians seeking causes and cures of vibration and noise in motor vehicles. Covers noise in internal combustion engines and their exhaust systems, engine mountings, crankshafts, rear axles, drivelines, brakes and brake discs, tires and roads, engine hum, and gear noise.

Sewage Sludge Treatment. Ronald W. James. vii + 276 pages. Noyes Data Corp., Park Ridge, N.J. 07656. 1972. $36, paper.

Information in the book is based on U.S. patents since 1960 relating to sewage sludge treatment. Covers activated sludge, wet oxidation, sludge dewatering processes (centrifugal, evaporative, filtration, flotation), incineration (fluidized bed and other processes), fertilizer (composting and compaction), flocculants, nitrate and phosphate removal, and general processes.

Salvage Markets for Materials in Solid Wastes. U.S. Environmental Protection Agency. xxi + 187 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1972. $2.75, paper.

Evaluates the markets for secondary materials. Provides industry by industry data on raw materials consumption and the mix between virgin and secondary materials use. Emphasis placed on paper, ferrous metals, nonferrous metals, glass, textiles, rubber, and plastics, but other materials discussed also.

Reverse Osmosis Membrane Research. H. K. Lonsdale, H. E. Podall, Eds. xi + 503 pages. Plenum Press, 227 W. 17 St., New York, N.Y. 10011. 1972. $27.50, hard cover.

Survey of current research covers the problems connected with membrane transport and indicates direction of future research. Topics include: theory of water transport and salt rejection by different membranes, analysis of concentration polarization problems, brackish and seawater desalting, new membrane systems, and cellulosic and noncellulosic polymeric and hollow-fiber membranes.

Population, Resources, and the Future: Non-Malthusian Perspectives. Howard M. Bahr et al., Eds. vii + 352 pages. Brigham Young University Press, Provo, Utah 84601. 1972. $3.95, paper.

Compilation of articles and papers written by renowned authorities in several sciences on the topic of population. Papers chosen with the intent of highlighting and documenting the point that the neo-Malthusian perspective on population growth and the attribution of social and environmental problems to overpopulation are only some of several hypothetical approaches to the total environmental problem.

Environmental Chemistry: Air and Water Pollution. H. Stephen Stoker, Spencer L. Seager. iv + 186 pages. Scott, Foresman and Co., Oakland, N.J. 07436. 1972. $2.95, paper.

Authors attempt to take an objective look at the problems of air and water pollution. Main focus is on the chemicals and chemical compounds involved, but there is some overlap into other scientific disciplines. Authors feel that most of the acute environmental problems can be solved with technology now available. However, the attitude of the public must be changed to accept the fact that they must pay the bills.

The Relationship of Land Use and Transportation Planning to Air Quality Management. George Hagevik, Ed. 287 pages. Center for Urban Policy Research & Conferences Dept., University Extension Div., Rutgers University, New Brunswick, N.J. 08903. 1972. $10, paper.

Papers cover the role of information in planning, planning air pollution control through the 60's, the perspective that must be taken for the 70's and beyond, the transportation component, and point and area sources in a planning context.

The Environmental Mercury Problem. Frank M. D'Itri. 124 pages. Chemical Rubber Co. Press, 18901 Cranwood Parkway, Cleveland, Ohio 44128. 1972. $27.50, hard cover.

Report from project initiated and passed during the 75th legislative session in Michigan in 1970. Covers the history, background concentrations, uses and sources, analysis, translocation, methylation, decontamination, epidemiology, and toxicology of mercury. Also covers a chronology of the world's mercury poisoning problem.

The Fate of the Lakes: A Portrait of the Great Lakes. James P. Barry. 192 pages. Baker Book House, 1019 Wealthy St., S.E., Grand Rapids, Mich. 49506. 1972. $14.95, hard cover.

Presents a portrait of the Great Lakes and explores the future possibilities for the Lakes and their impact upon the lives of Canadian and U.S. citizens. The author emphasizes ecological concerns but also covers navigation, shipping and ship building, commercial and sports fishing, power production, and recreation.

Response of Plants to Environmental Stresses. J. Levitt. xii + 697 pages. Academic Press Inc., 111 Fifth Ave., New York, N.Y. 10003. 1972. $32.50, hard cover.

Provides an analysis of the injuries produced in plants by physicochemical stresses (e.g., high and low temperature, water, radiation, salt, pollution), as well as the kinds of resistance plants develop against such stresses. Text and reference source for all phases of plant science as well as researches in industrial firms and environmental problems.

Air Pollution Control: Processes, Equipment, Instrumentation. Lexington Data, Inc., Box 311, Lexington, Mass. 02173. 1972. $250.

Report indexes and abstracts of 1400 U.S. patents issued from 1967 through 1971 on this subject. Of the 1400 patents issued, only 180 dealt with internal combustion engine emissions. For another example, only 52 of the patents were aimed at NO_x control.

Soil Geography. J. C. Cruockshank. 256 pages. Halsted Press, 605 Third Ave., New York, N.Y. 10016. 1972. $12, hard cover.

Besides emphasizing the dynamic nature of soil and the factors that influenced its formation, the author describes the history of man's relationship with the soil. Includes examples of soil pollution and the use and effects of fertilizers. Intended as a basic text, and also provides essential materials for the discussion of wider ecological questions.

Environmental Information Sources: A Selected Bibliography. Carole Schildhauer, Compiler. 45 pages. Special Libraries Association, 235 Park Ave. South, New York, N.Y. 10003. 1972. $3.80, paper.

Covers abstracts, bibliographies, catalogs, directories, handbooks, journals, newsletters, and other sources. Prepared for the Environmental and Ecological Literature—Where Does It All Come From? seminar held during the 63rd annual conference of the Special Libraries Association.

World Energy Supply/Demand During a Period of Crisis. 153 pages. Interdevelopment, Inc., Suite 814, Millard Fillmore Bldg., 2341 S. Jefferson Davis Hwy., Arlington, Va. 22202. 1972. $270.

Deals with the growing problems of energy demand and supply. Higher energy costs and increased competition for fuels, both among nations and among industrial segments within a given country, are to be expected. Covers North America, Latin America, Europe, Asia, and other nations.

Sowing the Wind. Harrison Wellford. xxiii + 384 pages. Grossman Publishers, Inc., 44 W. 56 St., New York, N.Y. 10019. 1972. $7.95, hard cover.

A report for Ralph Nader's Center of Responsive Law on Food Safety and the Chemical Harvest. Describes the use of various chemicals in food supplies.

Indicators of Environmental Quality. William A. Thomas, Ed. x + 275 pages. Plenum Press, 277 W. 17 St., New York, N.Y. 10011. 1972. $18.50, hard cover.

Examines indicators and indices which measure variables and provide overall composite values with which to assess the environment. Interdisciplinary reference work quantitatively evaluates the effects of ecological and technological processes. Leading authorities investigate underlying principles, design, and testing of indicators that describe environmental quality from social, physical, chemical, and biological perspectives.

Humic Substances in the Environment. M. Schnitzer, S. U. Khan. vii + 327 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, N.Y. 10016. 1972. $19.50, hard cover.

Discusses the principal organic components of soils and waters that participate in and control many reactions that occur in these environments. Presents an up-to-date account of the chemistry and reactions of humic substances. Of value for environmental students and scientists in areas of soil and water, biologicals, chemicals, geochemicals, and others.

Nutrients in Natural Waters. Herbert E. Allen, James R. Kramer, Eds. x + 457 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. $12.50, hard cover.

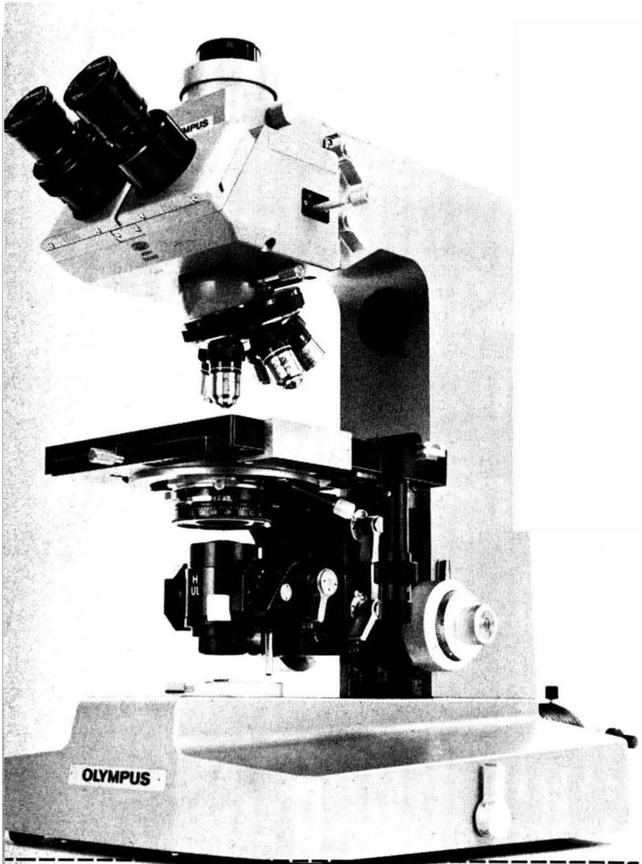
Broad coverage of all aspects of the chemistry, biochemistry, and geochemistry of nutrients. Information source for all researchers and policymakers involved in nutrient matters—water and water pollution, ecology, aquatic chemistry, biology, water resources, and water treatment. Can also be used as supplementary reading in graduate level courses in limnology and aquatic chemistry, oceanography, and ecology.

River Ecology and Man. Ray T. Oglesby, Clarence A. Carlson, James A. McCann, Eds. xvii + 465 pages. Academic Press Inc., 111 Fifth Ave., New York, N.Y. 10003. 1972. $11.50, hard cover.

Series of reports by scientists, engineers, and social scientists. Presents information on rivers and man's interactions with them. Intended for fishery biologists, aquatic ecologists, limnologists, sanitary engineers, hydrologists, systems analysts, aquatic chemists, administrators of water quality management programs, and other scientists and engineers concerned with the study and management of freshwater systems.

An Introduction to Air Chemistry. Samuel S. Butcher, Robert J. Charlson. xiii + 241 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1972. $10.95, hard cover.

Designed for those with no previous experience in the field, say the publishers, this book synthesizes the areas of chemistry and meteorology required to bring into focus some of the complex problems associated with the atmospheric environment. Authors also cover the topic of aerosols, an important topic in atmospheric chemistry.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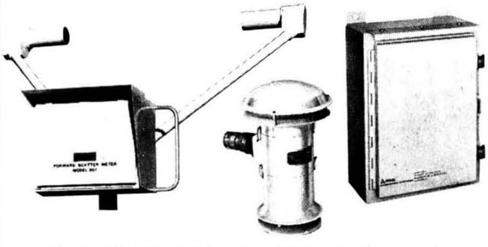
FORWARD SCATTER METER
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MEETING GUIDE

April 19 Virginia Beach, Va.
Third Commonwealth Air Pollution Control Workshop and Exhibit. State Air Pollution Control Board and Va. Port Authority.

A forum for exchanging environmental information, including new advances in air pollution control techniques. *Contact:* Tony Mason, Virginia Port Authority, 1600 Maritime, Norfolk, Va. 23515

April 23–25 Washington, D.C.
National Academy of Sciences. 110th Annual Meeting

Contact: National Academy of Sciences, 2101 Constitution Ave., Washington, D.C. 20418

April 23–27 Washington, D.C.
National Meeting on Complete WateReuse. American Institute of Chemical Engineers and EPA

Sessions will cover the broad topics of engineering, administration, economics, and public. *Contact:* Larry Cecil, Chairman, Water Section, Environmental Division, AIChE, 345 E. 47th St., New York, N.Y. 10017

April 24–26 St. Louis, Mo.
First ISA Joint Spring Conference. Instrument Society of America

Includes two air quality sessions and one water quality session planned. *Write:* F. J. Belcher, 1973 ISA J. C. Registration Chairman, P.O. Box 8435, Olivette, Mo. 63132

April 24–27 Chicago, Ill.
Iron & Steel Exposition & Convention. Association of Iron and Steel Engineers

Features strong pollution control program. *Contact:* Association of Iron and Steel Engineers, Suite 2350, Three Gateway Center, Pittsburgh, Pa. 15222

April 25–26 New York, N.Y.
Conference on Occupational Safety & Health Act. New York University.

Write: William A. Kulok, 600 Third Ave., New York, N.Y. 10016

April 25–27 Palm Beach Shores, Fla.
American Nuclear Society and Marine Technology Society. National Topical Meeting

Theme: "The Ocean, Nuclear Energy & Man," *Contact:* M. Jack Ohanian, Chairman, Dept. of Nuclear Engineering, University of Florida, Gainesville, Fla. 32601

April 26–27 Durham, N.C.
National Symposium on Ultimate Disposal of Waste Waters and Their Residuals. Research Triangle Universities and others

Sessions on land disposal, marine disposal, sludge handling, design practice, recovery, and recycling. *Contact:* F. E. McJunkin, Associate Director, Water Resources Research Institute, North Carolina State Univ., 124 Riddick Bldg., Raleigh, N.C. 27607

April 28 Chicago, Ill.
Second Annual National Symposium on Societal Problems of Water Resources. Illinois Earth Science Assoc. and American Water Resources Assoc.

Contact: Musa Qutub, Symposium Chairman, Northeastern Illinois Univ., Bryn Mawr at St. Louis Ave., Chicago, Ill. 60625

April 29–May 2 St. Louis, Mo.
National Association for Environmental Education. 1973 Annual Meeting

Write: National Association for Environmental Education, P.O. Box 1295, Miami, Fla. 33143

April 29–May 2 Houston, Tex.
Fifth Annual Offshore Technology Conference. American Institute of Chemical Engineers and others

Session topics include: environmental conservation, control of oil spills, remote sensing and navigation, and other subjects. *Contact:* Offshore Technology Conference, 6200 N. Central Expressway, Dallas, Tex. 75206

April 29–May 3 New Orleans, La.
American Oil Chemists' Society. 64th Annual Spring Meeting

Includes discussions on pollution abatement—control of dust, water, hydrocarbons, and proteins. *Write:* AOCS Headquarters, 508 S. Sixth St., Champaign, Ill. 61820

April 29–May 3 St. Louis, Mo.
Radiation Research Society. 21st Annual Meeting

Contact: Richard J. Burke, Jr., RRS, 4211—39th St., N.W., Washington, D.C. 20016

May 1–3 Lafayette, Ind.
28th Annual Purdue Industrial Waste Conference. Purdue University

Will cover numerous phases of industrial waste treatment through research, design, operations, and/or case history aspects. *Write:* David W. Hawkins, Civil Engineering Dept., Purdue Univ., West Lafayette, Ind. 47907

May 3–4 St. Louis, Mo.
1973 Composting and Waste Recycling Conference. Rodale Press, Inc., and Coalition for the Environment

Theme: "Using municipal wastes in agriculture." *Write:* Rodale Press, Inc., Organic Park, Emmaus, Pa. 18049

May 3–4 Washington, D.C.
National Academy of Engineering. 9th Annual Meeting

Write: National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, D.C. 20418

May 8 Paramus, N.J.
Third Annual Industrial Air Pollution Seminar. Rossnagel & Associates

Covers control equipment displays and papers directed toward engineers in textile, printing, plating, food processing, foundry, odor, acid, chemical, dust industries. *Write:* W. B. Rossnagel, Director, Rossnagel & Associates, 1999 Rt. 70 (E. Marlton Pike), Cherry Hill, N.J. 08003

May 9 Chagrin Falls, Ohio
4th Annual Engineering Your Environment Conference. Cleveland Engineering Society

Contact: Cleveland Engineering Society, 3100 Chester Ave., Cleveland, Ohio 44114

May 13–18 Las Vegas, Nev.
American Water Works Association. 93rd Annual Conference

Will cover water quality and distribution, research and resources, management and education, standards, industrial water, and engineering and construction. *Contact:* Harry Becker, AWWA, 2 Park Ave., New York, N.Y. 10016

May 14–16 San Francisco, Calif.
Technical Association of the Pulp and Paper Industry. 1973 Environmental Conference

Theme will be "Pollution Solutions," *Write:* B. G. Beeland, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

May 14–16 Athens, Ga.
Third Annual Symposium on Recent Advances in the Analytical Chemistry of Pollutants. EPA, Univ. of Ga., and others

Designed to bring together persons concerned with the application of analytical chemistry to the solution of environmental problems. *Write:* Rudi Seitz, Southeast Environmental Research Laboratory, College Station Rd., Athens, Ga. 30602

May 14–17 Philadelphia, Pa.
American Petroleum Institute. 38th Midyear Meeting of the Division of Refining

Sessions will cover pollution control and the nation's energy gap. *Write:* American Petroleum Institute, 1801 K St., N.W., Washington, D.C. 20006

May 15–17 Toronto, Ont., Canada
Second Annual Pollution Control Show. Pollution Control Association of Ontario

Conference will take a practical approach to pollution control in terms of economics and legislation. *Write:* Dianne C. Warnick, Public Relations Coordinator, Ontario Marketing Productions Ltd., 111 Bond St., Toronto 200, Toronto, Ont., Canada.

May 16 Indianapolis, Ind.
In-Plant, Out-Plant Pollution Control Symposium. Central Indiana Technical Societies

Write: Robert S. Bailey, Treasurer, AIChE–Indianapolis Section, 9620 Greentree Dr., Carmel, Ind. 46032

May 16 Toronto, Ont., Canada
Oil and the Canadian Environment. University of Toronto

Topics include sources of oil, effects, legal, social, and economic implications, surveillance and monitoring, and cleanup technology. *Write:* Mrs. J. Seddon, Institute of Environmental Sciences and Engineering, Haultain Bldg., Univ. of Toronto, Toronto, Ont., Canada.

May 16–18 Charleston, S.C.
Southern Environmental Resources Conference. Council of State Governments

Contact: Council of State Governments, Iron Works Pike, Lexington, Ky. 40505

May 18 Newark, N.J.
Spring 1973 Technical Conference. MASS-APCA

Topic will be "Ambient Air Monitoring Needs—Equivalency." *Contact:* Reuben W. Wasser, Public Service Electric and Gas Co., 200 Boyden Ave., Maplewood, N.J. 07040

May 20–25 Boston, Mass.
Annual American Industrial Hygiene Conference. American Industrial Hygiene Association and others

Conference will feature the latest in R&D in the field of worker protection. *Write:* E. Lynn Schall, Managing Director, American Industrial Hygiene Association, 210 Haddon Ave., Westmont, N.J. 08108

May 20–27 approximate Miami, Fla. and Jacksonville, Fla.
Lime Sludge Reduction and Color Removal Seminar. Permutit Co.

Contact: A. W. Pieper, Manager, Marketing Services, Permutit Co., E. 49 Midland Ave., Paramus, N.J. 07652

May 21–25 Boston, Mass.
American Industrial Hygiene Conference. American Industrial Hygiene Assoc.

Write: E. Lynn Schall, American Industrial Hygiene Assoc., 210 Haddon Ave., Westmont, N.J. 08108

May 22–24 New York, N.Y.
1973 Pollution Engineering & Equipment Exposition & Conference. Technical Industry Expositions, Inc.

Contact: Technical Industry Expositions, Inc., 34 W. Putnam Ave., Greenwich, Conn. 06830

May 22–24 Washington, D.C.
Environmental Impact on the Textile Industry Symposium. American Association of Textile Chemists and Colorists

Will cover environmental problems, solutions, and economics; government regulations; OSHA regulations; and action taken by the textile industry. *Contact:* AATCC Technical Center, P.O. Box 12215, Research Triangle Park, N.C. 27709

May 22–24 New York, N.Y.
Institute of Environmental Sciences. 19th Annual Technical/Tutorial Meeting and Equipment Exposition

Contact: Betty L. Peterson, Institute of Environmental Sciences, 940 E. Northwest Hwy., Mount Prospect, Ill. 60056

May 23–25 Chicago, Ill.
ISA Power Industry Division's National Symposium. ISA

Will cover NO_x abatement and its relationship to power plant operations. *Write:* Al Watson, General Chairman, Westinghouse Controls and Instrument Div., 10 S. Riverside Plaza, Chicago, Ill. 60606

June 3–6 Wichita, Kan.
20th National Watershed Congress. National Watershed Congress

"Land Use in Watersheds" is the theme. Discussions will center on the manner in which upstream watershed projects affect the use of land resources. *Write:* National Watershed Congress, 1025 Vermont Ave., N.W., Washington, D.C. 20005

June 3–6 Detroit, Mich.
American Institute of Chemical Engineers. 75th National Meeting

Contact: AIChE, 345 E. 47 St., New York, N.Y. 10017

June 3–10 approximate Baltimore, Md.
Waste Treatment Separation Concentration & Dewatering Systems Seminar. Permutit Co.

Contact: A. W. Pieper, Manager, Marketing Services, Permutit Co., E. 49 Midland Ave., Paramus, N.J. 07652

June 4–7 Fargo, N.D.
Symposium on Metal Toxicology and Coatings. North Dakota State University

Write: Zeno W. Wicks, Jr., North Dakota State Univ., Fargo, N.D. 58102

June 5–7 Montreal, Que., Canada
Third Annual Conference on Pollution Control in the Marine Industries. International Association for Pollution Control

Will cover marine pollution prevention in the Great Lakes, coastal states, and the Arctic. *Contact:* Meltem Orer, IAPC Headquarters, 4733 Bethesda Ave., Washington, D.C. 20014

June 11–14 Dayton, Ohio
Workshop on Environmental Problems in the Extractive Industries. Geological Society of America and others

Aimed at generalists and specialists involved in resource extraction, mineral processing, pollution, law, and waste handling. *Write:* Raul A. Deju, Workshop Coordinator-Geology Dept., Wright State University, Dayton, Ohio 45431

June 11–14 Burlington, Ont., Canada
Remote Sensing of Water Resources International Symposium. AWRA and Canada Centre for Inland Waters

Will cover water resource applications of airborne remote sensing and satellite-borne sensors and the role of remote sensing in integrated water resource management systems. *Write:* American Water Resources Association, 206 E. University Ave., Urbana, Ill. 61801

June 17–22 Amherst, Mass.
American Institute of Biological Sciences. 24th Annual Meeting

Write: Ann F. Kulback, AIBS, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016

June 18–21 Oxford, Ohio
Paper Technology Symposium. Miami University

Covers air and water quality improvement through monitoring systems. *For additional information:* Miami University Paper Technology Dept., Oxford, Ohio 45056

June 18–22 Mexico City, Mexico
American Association for the Advancement of Science. Annual Meeting

Contact: AAAS, 1515 Massachusetts Ave., N.W., Washington, D.C. 20005

June 20 Storrs, Conn.
Wetland Conference. University of Connecticut

Write: T. Helfgott, University of Connecticut, Storrs, Conn. 06268

June 20–22 Columbus, Ohio
1973 Joint Automotive Control Conference. AIAA, AIChE, ASME, IEEE, ISA, TAPPI, ITE, and SCi

Conference will emphasize application to societal, economic, ecological, and biological systems. *Contact:* ASME, 345 E. 47 St., New York, N.Y. 10017

June 22–23 Dayton, Ohio
Fifth Ohio Valley Gas Chromatography Symposium. Ohio Valley Gas Chromatography Discussion Group

Contact: Ohio Valley GCDG, Attn: Jean Weaver, Station B, Box 8, Dayton, Ohio 45407

June 24–28 Chicago, Ill.
Air Pollution Control Association. 66th Annual Meeting & Exhibition

Contact: Daniel R. Stearn, APCA, 4400 Fifth Ave., Pittsburgh, Pa. 15213

Courses

April 26–27 Madison Wis.
Special Topics in Sanitary Landfill. University of Wisconsin

For engineers, planners, public works and governmental officials, and waste management system supervisors and operators. Fee: $95. *Contact:* Thomas P. Kunes, Solid Waste Management Specialist, Univ. of Wis.-Extension, 432 N. Lake St., Madison, Wis. 53706

May 3–4 New York, N.Y.
Market Opportunities in Environmental Control & Safety. Predicasts, Inc.

Seminar will cover more than 100 opportunities in environmental control and safety. Fee: $250. *Write:* Predicasts, Inc., 200 University Circle Research Center, 11001 Cedar Ave., Cleveland, Ohio 44106

May 21–25 Washington, D.C.
Mathematical Models for the Environmental Sciences. George Washington University

Fee: $335. *Contact:* Continuing Engineering Education Program, George Washington Univ., Washington, D.C. 20006

May 21–25 Bronx, N.Y.
18th Summer Institute in Water Pollution Control. Manhattan College

Two one-week courses offered concurrently in: biological waste treatment and mathematical modeling of natural water systems. Fee: $250. *Write:* Donald J. O'Conner, Environmental Engineering & Science Program, Manhattan College, Bronx, N.Y. 10471

May 21–25 Rolla, Mo.
Water Pollution Control. University of Missouri–Rolla.

Designed for engineers and scientists associated with consulting, industrial, educational, and governmental organizations with an interest and responsibility for water pollution control. Fee: $250. *Contact:* Extension Division, University of Missouri-Rolla, Rolla, Mo. 65401

May 31–June 1 Washington, D.C.
Advanced Wastewater Treatment. South Tahoe Public Utility District and others

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